Report of the Workshop on

The Next Generation of in situ Biological and Chemical Sensors in the Ocean

held 13-16 July 2003

Executive Summary

Long-term, high-resolution measurements are necessary to improve our understanding of biogeochemical processes from coastal to deep-sea environments. The sensors workshop held in Woods Hole, July 2003 documented critical scientific and engineering aspects of existing, emerging, and proposed sensors in oceanography. Engineers and scientists in attendance represented a broad range of fields from biological and chemical oceanography, fisheries oceanography, homeland security, mining, space exploration, military, nanotechnology, remote sensing, fluid dynamics, and medicine providing a unique forum for exchanging ideas and fertilizing new concepts. Among some of the exciting advances discussed were in-situ optical spectrophotometry, mass spectrometry, voltammetry, and laser induced breakdown spectroscopy (LIBS) for measurement of elemental composition, trace metals, nutrients and dissolved gases. Novel, nucleic acid sensors for measuring the abundance of specific genes and gene products (DNA, RNA) were highlighted for species identification. Integration of various sampling modalities will be necessary to nest different measurements and provide appropriate resolution on various time and space scales. For example, optics and acoustics together represent a powerful tool for characterizing particulates, plankton, fish and whales in the ocean. The Autonomous Vertically Profiling Plankton Observatory was provided as an example of how to fully integrate biological, chemical, bio-optical, and physical measurements to address specific scientific questions. Scaling issues will require large area sensor arrays to be designed for long term, autonomous operation. Workshop recommendations highlighted the need to develop sensors capable of extended deployments with fast response, high accuracy and precision, wide dynamic range, self-calibration, low power consumption, common interface, and cost effectiveness. Rapid advances in miniaturization, sensor integration, and enhanced embedded computing power through micro and nanotechnology can fuel the development of the next generation of oceanographic sensors. High-volume production of intensively integrated sensor systems will reduce costs and enable deployment throughout the global ocean. The research community needs to establish centers to act as a clearing house for information on sensor development, to provide a sensor failure-reporting system, standardization of communications, power, and physical connections, calibration, maintenance and training, and evaluation of instruments for sufficient robustness for operation in remote, harsh environments. Educating the next generation of engineers and technologists in sensor design and operation is essential to long term success in oceanography. Sustained funding for sensor development and their transition into mainstream oceanography is critical to the success of proposed observing systems.

Introduction

New and improved sensors are required in the ocean environment for sustained, autonomous measurements on remote observatories. This report describes the results and recommendations of the July 2003 workshop on The Next Generation of *In Situ* Biological and Chemical Sensors in the Ocean which focused on new developments in primary sensor technologies. The next generation of sensors will allow scientists to address a suit of critical interdisciplinary questions based on long term, high resolution measurements of biological and chemical properties of the ocean.

The sensors workshop sought to bring together oceanographers and specialists in new and emerging technologies which could be used for the in situ oceanographic biological and chemical measurements of the future. Examples of technologies explored included nanotechnology, sensor arrays, miniaturized complex instrumentation (e.g. mass spectrometers), automated complex chemical analyses (e.g. DNA analyzers), biosensor arrays, and new high resolution optical visualization tools. The major questions addressed were: What are new technologies and innovations emerging in the fields of engineering, analytical chemistry, biosensors, and molecular biology which would be useful in addressing major outstanding scientific problems in oceanography? What are the technological barriers to applying these technologies and how can these be overcome? The workshop sought to maximize interactions between oceanographers and specialists in other technical fields which might lead to conceptualization, development, testing, and deployment of new and innovative technological approaches in ocean sensor technology.

Important workshops leading up to this one include the Scientific Cabled Observatories for Time Series (SCOTS) and the Autonomous and Lagrangian Platforms and Sensors (ALPS).
Both reports described how Eularian and Lagrangian time series measurements will be used to address specific questions, and how sensor design, performance and integration could limit vehicle and observatory performance. Throughout the SCOTS and ALPS reports, there were common, but specific calls to develop sensors for critical measurements that are not possible with current technology, and to ensure new sensors are designed keeping in mind the requirements for both autonomous and cabled platforms.

The sensors workshop was designed to meet this call by providing a forum for exchange of ideas between scientists and engineers who may not necessarily be working in the field of oceanography. Attendees represented a broad range of fields from biological and chemical oceanography, fisheries oceanography, homeland security, mining, space exploration, military, nanotechnology, remote sensing, fluid dynamics, and medicine. The diversity of interests provided a unique experience for participants while infusing new directions to sensor design in oceanography.

Most importantly, findings and recommendations for new sensors provided by SCOTS and ALPS parallel those of this report from the Sensors Workshop. Thus, the scientific community is finding convergence on how we define and make critical decisions relative to sensor design and implementation on a variety of platforms.

Overview
The sensors workshop was organized into one and a half days of oral presentations followed by one day of breakout groups. Three overview talks addressing critical science questions set the stage for 26 technical talks describing both existing and future developments in biological and chemical sensor design and application. Working groups were broken into two Phases: Phase I addressed scientific requirements for existing and novel sensors while Phase II focused on technological development necessary to meet the science objectives.

During Phase I, working groups addressed the following issues:
Population density and community structure
Health- Metabolism, and Physiological Processes
Behavior
Processes occurring at the Air-water interface
Processes occurring at Vents and seeps
Processes occurring in the water column
Processes occurring at the Sediment-water interface

Questions posed to the working groups included the following:
1. In your particular field, what are the critical scientific questions and properties need to be measured?
2. What are the critical temporal and spatial scales, accuracy, and resolution for measurement of these properties?
3. What are the requirements and limitations of existing sensors in terms of temperature, pressure, depth range, and potential for in situ long term use, power requirements, adaptability to high salinity aqueous environment, data processing and transmission requirements, adaptability for multiple rapid in situ measurements, and other factors required or desired for use in the open ocean?

During Phase II, the issues addressed were:
Remote detection of organisms and chemicals
Motion tracking of organisms and particulates
Dissolved gases in the water column
Inorganics in the ocean
Organics in the ocean

Questions posed to the working groups included the following:
1. Considering the important scientific questions raised in Phase I working groups, what refinements should be made on existing sensors to make them more suitable for long term in situ use for open ocean monitoring?
2. What new sensors need to be developed?
3. What are the functional requirements of the sensors needed to make these measurements: i.e. resolution, accuracy, response time, stability, calibration, resistance to bio-fouling, size, weight, buoyancy, sensitivity to acceleration, temperature, pressure,

humidity, and UV light.

Themes and Conclusions

Population density and community structure

Important questions identified were: 1. What species and populations are present and how do they change over time? 2. What is the character and variability of the co-located physical environment (habitat) and how does the organism/population respond to environmental change? 3. At what level are populations not uniform? 4. How does the community and population structure change over temporal and spatial scales? 5. What are the important taxa (indicator species) and biological events to target in various ecosystems? 6. What controls the distribution and abundance of marine organisms (viruses to whales?). To address these questions we need to understand biologically relevant scales from the perspective of the organism, to basin scales controlling community structure. High density basin scale multi-sensor platforms will lead to an understanding of "local" ecology in context with large scale forcing. How do we integrate systems that have nested observations? Deployment strategies become critical to the understanding of population-scale questions. Techniques are needed for automated species-level identification using molecular probes combined with optical imaging and acoustic systems to cover appropriate scales. For example, use acoustics to sample 10s of meters to m scale, optics to sample m to μm scale and then take discrete samples for analysis of genes and gene products (e.g., DNA, rRNA, mRNA, protein, lipids). Such sensors would be integrated to produce a complete system capable of quantifying a wide range of planktonic organisms while deployed on a variety of observatories including profiling moorings, AUVs, ROVs, and Lagrangian platforms. Adaptive sampling capability ids essential for understanding event processes, such as alterations in community structure in response to chemical and physical forcing.

Health- Metabolism, and Physiological Processes

Critical questions relate to in situ measurements of 1. Condition state, such as metabolism, feeding rate, stressors for fish, zooplankton and microbes; 2. Heterotrophic production, such as growth rate, reproductive rate and mortality rate; 3. Gene expression for rate processes. The overall challenge is to develop a capability for predicting the potential for growth and reproduction using a condition proxy such as activities of specific biomolecules like extracellular bacterial enzymes and copepod digestive enzymes. Miniature analytical systems that meet some of these functional requirements are under active development and in some cases are already commercialized for biomedical applications. Bringing these advancements to bear on autonomous platforms applied to environmental research and monitoring requires sample collection and processing schemes that differ from those currently used or envisioned for biomedical tests. In the near future, small molecular diagnostic devices will probably not provide data rates comparable to chemical and physical measurements, like those possible with conductivity or temperature sensors. Therefore, near term application of biosensors fielded on autonomous platforms will likely be tightly integrated with, and to some extent controlled by, other sensors that trigger a molecular analytical event in response to environmental gradients readily detectable at high frequency.

Behavior

The major questions addressed in the behavior working groups included: 1 How do we count and measure fish or other organisms in a quantitative way? 2.How do we use behavior to make more effective use of the sampling tools available? 3. How do animals discriminate useful signals from noise? 4. Can chemicals be used to predict/measure behaviors such as spawning activities? The use of good behavioral rules are important when implementing a sampling program. The sampling routine should be continuous and systematic: Martin and Bateson 1996. Measuring Behavior. Cambridge Univ. Press. Is a good example of how to implement effective sampling strategies that take into account the behavior of the organism. The dynamic range of sensors needs to be increased. Lasers, multispectral optics, and low frequency acoustic absorption techniques can provide more information at increased resolution and/or range. Multiple sampling tools operating at complimentary scales need to be integrated to verify sensed data. A major challenge is to increase sample volume while continuing to quantify the environment on scales of animals within the volume. Organisms respond to chemical cues in the water such as squids initiating spawning behaviors in mass. In some cases, odors could be used to identify natal habitats; However, we generally don't know what the chemicals are. Chemical techniques such as RAMAN spectroscopy and LIBS described elsewhere in this workshop should be considered for in situ behavioral studies.

Processes occurring at the Air-water interface

The transfer rate of individual gases across the air-sea interface is a major unknown in estimating where the ocean is acting as a sink or a source of carbon dioxide and other ecologically and climatically important gases. These transfer rates, especially for CO2, are also important in constructing and validating global climate models. The magnitude and rate of gas transfer is strongly influenced by a microlayer at the air-sea interface. Knowing the rates of change in individual gases across the microlayer would be a huge advance which would be accomplished with innovations in measurement of the Eddy co-variance flux for all the oceanic biogeochemically important gases (e.g. oxygen and methane). In situ gas sensors which currently exist are too slow and unable make in situ measurements on the rapid time and space scales required to measure this flux. A new sensor package is needed which can measure in situ gas concentrations on smaller spatial scales (10uM) and at higher speed (100 Hz for CO2, for example)

Processes occurring at Vents and seeps

Some critical scientific issues regarding vents and seeps are: What are the biogeochemical interactions that control/influence life and metabolic processes at vents and seeps? What are the temporal and spatial variations in geochemical and thermal fluxes (seconds-years)? What are the linkages between vent and seep fluxes and the underlying (hydro) geology? How do we investigate recharge on ridge axes/flanks? What are the real primary fluid chemistries issuing from vents and seeps if measurements could be made with no chemical or physical interference by the sampling or measuring process itself?

Some of the limitations of existing sensors are their inability to follow the rapid chemical and biological changes in both cold seeps and hydrothermal vent environments. The high temperatures and corrosive nature of hydrothermal vent fluids currently almost precludes use of in situ sensors. For cooler seeps <70^{o}C, biofouling becomes a problem. In addition, some scientific questions about seafloor vent and seep environments cannot be addressed because the sampling procedure itself perturbs the system. For example, physical changes arising during fluid sampling at vents and seeps, such as temperature and pressure drops and precipitation, can lead to incorrect conclusions about the nature of the earth's deep subsurface. There is a much better chance of avoiding these problems with in situ measurements as close as possible to the site of venting.

Sensors requiring progressive development: Chemical sensors need to be designed to operate in the harsh chemical environments plumes as well as in cold seeps and at the interfaces between fluids and mineral surfaces at vent chimneys. One particularly useful mechanism of sensor deployment would be event-triggered sampling whereby measurements are designed to commence with the start of unusual seismic activity, or uncharacteristically anomalous changes in vent fluid or seep chemistry, relative to steady state conditions, as monitored by some robust continuous monitoring device. Achievement of this goal requires major advances in process control and signal processing instrumentation. A means to mitigate corrosion effects at vents would be to use time-limited deployments. A robotic device could perform the measurement with an attached infrared sensor to help locate the highest temperature fluid. Following exposure sufficient to gather requisite data, the sensor would be withdrawn. This procedure could be repeated as needed to constrain key aspects of the temporal evolution of the hydrothermal system.

Processes occurring in the water column
Mathematical models of processes (turbulence, thin layers, stratification) need to be validated with field data which requires in situ measurements, sometimes continuously on small scales. The relative importance of vertical versus horizontal transport of energy and materials is currently poorly known. Little is known about lateral exchange including mechanisms of transport and transformation of chemical and biological materials. Information obtained in a nondestructive way is required on processes affecting both living and nonliving particles. For example, how do we predict when plankton is part of the food web versus dying and sinking to the ocean floor? These processes strongly effect oceanic carbon flux, important to both ecosystem health and to climate change. What are the *in situ* sinking speeds and flux rates of particles which bring nutrients and energy to the deep-sea? Present methods disagree by a factor of 2.

There is currently no way to measure negative flux – particle upwelling, such as that which occurs by resuspension of bottom sediments or productivity originating from the bottom rather than the top of the ocean such as that which occurs in vents and seeps. What are the effects of bottom seeps and rapid ground water discharge into coastal and slope environments? What are the effects of bottom fluid and gas venting on ocean productivity from the ocean bottom? What elements important to the ecology and health

of the ocean are transferred upward along with bottom gas and fluid venting? What is the fate of free gas venting as bubbles up into the water column?

Other important open questions about the carbon cycle in the ocean are: Is the concentration of phytoplankton changing? If so, is the change changing basin wide? What are the regional scales and importance of coastal vs ocean waters? What changes in carbon input, nutrients and maintenance (or not) of the steady state are the important controls? Is the "background ocean" changing as a result of anthropogenic impact? How are trace elements/metals affecting the biology and biological transformations? What is the critical mix of organic and inorganic chemical species needed to give a complete picture of the important biological processes and transformations? New production estimates are needed along with their relation to nutrient recycling in euphotic zone. What comprises the huge pool of high molecular weight organic matter in the ocean? How fast is it biodegraded? How much is available to oceanic biological communities and how does it relate to efficiencies and time scales of carbon production and cycling?

Smaller scale measurements are needed to study planktonic influences on carbon dynamics in ocean. How do various chemicals affect biological reproduction (mating)? Satellite data is needed to view overall phytoplankton populations during cloudy days. How can depth information be obtained from satellites? Can *in situ* sensor and satellite information be combined to get this information? How much light is being absorbed and used during photosynthesis? Photosynthesis (primary production), O_2, pCO_2, and pH data are needed at high spatial and temporal resolutions.

How can anoxia problems in the ocean and along the coast be documented and predicted? How do these relate the health of the ocean, such as recent episodes of Red Tide?

Many important physical processes occur on decadal time scales with slow chemical and biological responses. How can changes on many different time scales be tracked simultaneously?

Most existing sensors cannot rapidly measure changes on small and continuous scales to produce water column profiles with the detail currently obtainable from CTD profiles which record important spikes in concentration such as fluorescence anomalies caused by the presence of organisms. There is a critical need for adaptive event driven sampling and for in situ sensors to track and monitor processes in difficult environments which cannot be studied in other ways. For example, anoxia events are usually accompanied by increases in highly reactive sulfur compounds. Specific high sensitivity sensors are needed to measure the very small amounts of chemicals which affect biological reproduction and mating.

For many existing sensors, background data are needed for the specific area being examined. For existing sensors which fail often, such as those for O_2, Nitrate, transmissometer, epsilon (turbulence, acoustics), there is a need to deploy sensors frequently (every 2 weeks). How can this be accomplished without using ship deployments and without polluting the ocean with broken sensors? How can depths of

phytoplankton layers be gained from satellite data? Satellite data monitoring of phytoplankton in the ocean is not possible on cloudy days.

Sensors requiring progressive development: Some sensors should be suitable for long-term deployment to measure cyclical changes. In the near shore, there is a particular need for high density annual data which is critical for monitoring ecosystem health (wellness). Long-term rugged sensors need to be developed over the next 10 years that can measure nutrients, O_2, pH, CO_2, metals, H_2S, biological parameters at 1% accuracy, 1 % precision per second, N_2O and metals. There is a great need for a standard affordable sensor package that could be used to monitor most of these parameters in 3rd world countries.

Sensors requiring a quantum leap in development: To make major advances, a system approach is needed which combines sensors or uses a combined sensor to examine the physics, chemistry and biology of a particular part of the ocean. Integrated sensor packages need to be developed to measure a number of parameters simultaneously possibly on a variety of spatial and temporal scales from very short (mm) to basin wide. For example, how can point measurements be extrapolated to understand phytoplankton production and destruction in the entire ocean? In addition, simultaneous measurements on a number of species on a number of different time and space scales may be required. For example, the time varying nature of the C cycle has been the scientific theme of several past workshops. Sensors provide a potential means to track all of the important changes simultaneously and would serve a number of other purposes as well, allowing: 1) validation of mathematical models of rapid processes requiring continuous in situ measurements on small scales (examples: turbulence, formation of thin layers, stratification); 2) measurement of mesopelagic processes on short time and space scales; and 3) higher resolution measurements of vertical processes providing a window on episodic or abrupt changes in concentration caused by, for example, the presence of biological communities.

There is great need to track chemical and biological changes of particles in a nondestructive way on small scales over various representative areas. Possibly, the sensors of an organism could be used to advantage in cases, particularly where high sensitivity and high specificity are required, such as monitoring biologically produced chemicals which cause changes in behavior, e.g. sexual and mating behavior.

Simultaneous modeling and in situ measurements of specific small volumes of water ("Lagrangian cubic meter") would allow a determination of effects of various physical forcing processes. An example is how turbulence caused by storm events influences changes in important chemical and biological constituents.

Processes occurring at the Sediment-water interface

Very little is currently known about fluid migration from bottom sediments into the ocean bottom waters from any process other than diffusion. What is the importance of carbon and nutrient delivery from other more rapid processes including mixing and irrigation, resuspension, and material delivered through vents including hydrothermal vents, "cold seeps", and subsurface discharge of land-based run-off including pollutants? What are

effects of bottom seeps and rapid ground water movement into ocean? What are the effects of bottom fluid and gas venting on ocean productivity from the bottom? What elements important to the ecology and health of the ocean are transferred upward by bottom gas and fluid injection? What is the fate of free gas venting as bubbles up into the water column?

What is the relative importance of resuspension versus burial of organic carbon and nutrients? What is the fate of organic carbon in marine sediments? A considerable amount of organic carbon is "missing" in the global carbon budget. How much primary production occurs in the nephloid layer in near-bottom sediments, rather than in surface waters? Currently only surface processes are generally thought to be important in primary production. Is this correct? Finding and characterizing subsurface ground water and gas plumes is a technically challenging and important problem - these provide rapid delivery of fresh water, metals, nutrients, and pollutants to the ocean. A critical potential issue in all surface sediments is chemolithotrophy - what are the identities of organisms responsible for the associated chemical and biochemical changes?

The role of surface sediments in the global nitrogen cycle is currently an important unknown. What is the relative importance of denitrification and what is its mechanism? What is the fate of terrestrial organic matter in the ocean?

Many sensors exist for carrying out in situ measurements in the water (see water column summary above); there are very few in situ sensors for sediments, particularly for coarse sediments which are the most important site for movement of fluids, carbon, nutrients, and pollutants through the interface. Voltammetry is most promising given its ability to detect a variety of chemical signatures simultaneously. UV-Visible spectroscopy has some difficulties in sediments, but these are not insurmountable.

Sensors requiring progressive development: Voltammetry and UV-Visible spectroscopy require enhanced development given their initial promise. Radon is used as a tracer of water input from sediments. The building of an in situ pumping system to find radon for long-term seep monitoring was proposed. In situ measurements of chemicals and biochemicals associated with nitrogen budget are a critical need. To monitor and understand diagenesis of organic matter at the sediment-water interface, imports and exports of carbon to the ocean are important to measure. Time series instruments are needed for monitoring sediment pore waters - none currently exists. Some important carbon-cycle related measurements can only be done in real time. The data also needs to be transmitted in real time, for example that for the pH/biocarbonate related parameters in pore waters. For monitoring of these sensors in pore waters, there is a need to transmit data in real time as it is collected because short term changes which occur as the sample stands. Sediment variability even over small distances generally makes reproducible revisits and resampling impossible, making in situ sediment and pore water measurements a requirement. New methods are needed for chemical characterization of intractable organic matter (DOC, kerogen, etc).

Sensors requiring a quantum leap in development: There are many critical issues related to measuring sediment and particle fluxes which would benefit from instrumental innovations. An instrument is needed which can measure many particles simultaneously over time. With a large number of measurements, statistics of distribution could be performed. There is a critical need for "in situ multisensors" or sensors which can measure a number of different properties simultaneously. In situ versions of promising new methods need to be developed including in situ mass spectroscopy which would allow quantitative measurement of a number of volatile organic, biochemical and pollutant compounds simultaneously; scanning fluorescence which is an extremely sensitive technique for "fingerprinting" complex dissolved organic matter in the ocean; and LIBS, a very promising method for detecting and measuring multiple elements in situ in sediments, on particles, and possibly in the water column.

Remote detection of organisms and chemicals

The group worked on remote detection and measurement of organisms and water properties. Combinations of optics (holography, LIDAR, imaging), acoustics (200 KHz-3 MHz; low frequency absorption tomography) and satellite sensors for simultaneous measurement together with pCO2, oxygen, particle concentration to achieve sensor fusion was considered a priority. It will be necessary to use all these instruments and integrate the information to get more of an overall, multi-scale picture of the environment. The group described seven important points: 1. Calibration was recognized essential for ensuring quality of the data. Self-calibration procedures are necessary, especially for autonomous sensors. 2. Coherence in observations: want to pay attention to spatial and temporal co-incidence and overlap and the possibility of complementary uses of the data. For example, use near range optical sensing for identification and extrapolation to larger scales by means of longer range acoustics. 3. Integration of multiple sensors -- major increase in information to be gained for a modest increase in deployment. Sensor integration will provide a much more complete picture of the volume around observatories. 4. Power limited systems. Noted potential gains from consolidation, but need to remember performance tradeoffs in sharing cpu's and other finite resources. Also another trade-off, sensor technologies not mature and want to keep modularity for quickly evolving technologies. 5. Certification of instruments in atmospheric chemistry. 6. Platform compatibility of instruments. 7. Transitioning a research tool to operations was seen as a bottleneck for many prototype sensors. Funding opportunities are necessary to allow more rapid transition to community.

Motion tracking of organisms and particulates

How do we measure individual behavior and physics at the local scale as it forces patch dynamics? This question is sample size dependent: Optical tracking is optimal in volumes 1 m3 or less while acoustics is better for larger volumes. Combination of modalities would be ideal (e.g., Fish TV). Progressive development is working towards higher resolution imaging systems (16kx16k) to achieve micron resolution in a 1 m3 volume, decreased power requirements for illumination, image compression and real-time data processing on large images, and 3D stereo in real-time. Quantum leaps in development will allow designing the Nanopod, a biology inspired nano-robotic copepod capable of swimming and sensing its environment. This would use reverse engineering of copepods

to develop specifications of copepod's sensory system. The Nanopod would be designed to test specific hypotheses about how behavior influences vertical and horizontal distribution, and predator/prey/physics interactions. Tracking through interfaces with disparate refractive indices is seen as a major challenge which could be meet through both optical and software solutions.

Dissolved gases in the water column

Only a few oceanic in situ gas sensors exist today; none measure up to the following ideals: 1) In situ dissolved gas measuring instruments require ruggedness, high sensitivity and selectivity, low susceptibility to fouling/drift, and ability to become commercially available, through development, at appropriate costs (low cost = <$5K; best if <$100 for wide deployment), appropriate time response characteristics, low hysteresis, small form factor, low power consumption (1 yr = 1 W).

2) Modularity is important for ease of replacement and ability to swap units between platforms where appropriate. Power supplies and signals, etc., need to be standardized. It is crucial to have good communications between people building current instruments, those designing the next generation of sensors, and those involved in planning and building deployment strategies.

3) Ideally, response time would be rapid. Response times of instruments incorporating membranes are limited by the time it takes for gas in the dissolved gas phase to equilibrate with that in the dissolved aqueous phase.

4) The required response time characteristics of a sensor need to be well defined and built into a particular sensor. For example, a pumped CTD has a well-defined response time, compared to a self-flushing CTD. This knowledge can be used to optimize the system for a particular application.

For gas sensors, the following technologies are available but require refinement as described: For total dissolved gas measurements, there are gas tension devices which measure pressure); better time response (now 5-10 min.) and anti-fouling are needed. All of the present day in situ oxygen sensors have limitations. Nitrogen is generally calculated indirectly using oxygen measurements. For carbon dioxide measurements, both spectrophotometric and gas phase equilibration techniques are used, sometimes in combination. These techniques are slow and subject to drift. Recently, in situ carbon dioxide measurements have been carried out by Raman spectroscopy utilizing a fiber optic probe directly in contact with the water. Existing Gas sensors which would be extremely valuable for oceanographic work but require substantial refinement include methane, hydrogen, hydrogen sulfide, and radon sensors.

Other important gases for characterizing ocean processes for which sensors need to be developed include: the inert gases argon, neon, and helium; C2-C4 hydrocarbons; the nitrogen oxides; halocarbons including freon; bromine, mercury, sulfur gases; and sulfur hexafluoride which is used to track the distribution of chemical and biological species by tracer release experiments. Indirect methods for in situ detection of dissolved organic carbon and pH would be very useful and could involve chemical conversion to gas.

Sensors requiring progressive development: Some existing instruments which could be adapted for general deep ocean work include: In situ mass spectrometer – needs sample handling, power improvements, miniaturization. Raman spectroscopy – needs miniaturization, improved sensitivity and lower power requirements. Near IR/IR – requires ruggedization and better reproducibility and further development via evanescent wave spectroscopy. Laser induced breakdown spectroscopy (LIBS) is a very promising new technology for in situ and sensitive multi-element measurement adaptable to all phases. The instrument would require development of calibration methods of calibration and innovations in data handling to make the data quantitative. Fluorescence spectroscopy – need probes selective for more reagents. There is a need for faster and more selective membranes as well as a membrane selective waveguide, resistance to biofouling resistance, and in situ means of membrane replacement during long deployments. Multiple quantum well tunable diode lasers which can tune into fundamentals of materials are necessary. In situ membrane replacement technology is needed. Innovations are needed in satellite measurements, particularly better ways of reducing inference from dissolved gases.

Inorganics in the ocean

Processes requiring inorganic in situ measurements are described in the sections on water column processes, sediment-water interface and vents and seeps working group reports and summaries. Many sensors exist today. Most have been found to have limitations when used in the ocean and are not suitable for longer term deployment without modification. The CTD is considered today's "gold standard" of what is expected on an in situ sensor measurement in terms of instrumental robustness and resolution capabilities.

Sensors requiring progressive development: Development is needed for reliable in situ sensors to continuously measure and monitor all of the important nutrients in the ocean. New sensor technology should be based on the well developed laboratory chemistries that already exist for the many elements and could include the SEAS long path-length spectroscopy system. In situ ion selective electrodes would be useful in the differentiation of water masses. In a number of cases, existing in situ sensors are not very robust and require further development. In some cases, new wet-chemistries and colorimetry are needed for a number of metals. **C**hemiluminescent, gas-phase measurements, and biosensors are needed.

The highest priorities are to develop robust in situ methods for short and long term monitoring of ammonia/silicone, nitrate and other nitrogen compounds involved in marine nitrogen budgets, oxygen, and pH. Also needed, but at a lower priority, are short term sensors for iron as well as long and short term sensors for dust. In some cases, such as for iron, electrochemical method show promise

Sensors requiring quantum leaps in development: A multi-sensor array approach would be useful in solving a number of oceanographic problems, including particle classification. A very promising new procedure for simultaneous measurement of a variety of metals and other elements would be preconcentration combined with LIBS.

The procedure is potentially applicable to in situ analysis of dust and to identification of mineral phases in particles and sediments.

In situ methods are needed for measuring "tracers" of water column processes and particles, including hydrogen peroxide, and tracers of carbon export (radionuclides, ^{234}Th, ^{222}Rn, and Iodine).

Organics in the ocean
Very few in situ sensors to analyze organic compounds in the ocean are currently available. Exceptions are instruments involving absorbance and fluorescence spectroscopy of complex organic matter, including multiple wavelength SAFIre instrument and CTD plug-in modules to monitor specific groups of compounds, such as chlorophyll from phytoplankton. These CTD modules are limited because the signals are not specific to one group of molecules or organisms.

We need to develop sensors with specificity for one compound or a defined group of compounds. We also need instruments capable of surveying a variety of different compounds during ocean exploration, such as mass spectroscopy and Raman spectroscopy and rapid chromatographic methods.

There is a particular need to develop an integrated sensor for parallel in situ measurement of multiple organic acids and gases associated with specific communities of microorganisms, such as those in various redox zones including bottom waters and surface sediments. Such a system might include a mass spectrometer, one of more enzyme based probes, and a microfluidic device acting as a miniature high pressure liquid chromatograph (HPLC).

In situ fluorometry for specific pigments exists but needs further development, possibly in signal processing, to improve selectivity. Also, sensitive methods are needed for analysis of high molecular weight organic matter in organisms, on particles, and in bottom sediments. Scanning fluorescence, LIBS. and an instrument combining a series of specific bio- and chemical sensors are promising technologies which should be developed. Photoacoustics – laser probe, acoustic detection – should be explored for specific compound measurement. Specific sensors would be valuable for a variety of anthropogenic compounds including polycyclic aromatic compounds derived from automobile exhaust and storm sewer run-off, pesticides, surfactants, freons, etc.

There is always a trade-off between carrying out specific analyses versus bulk properties. Combined in situ sensors to do both as well on the same sample or in the same place would be ideal. Ability to measure in situ isotopic 13C ratios on specific molecules, particularly hydrocarbon gases such as methane, would be a major break-through in tracking oceanic fluid flow around ocean vents and seeps.

Probes currently exist for measuring proteins. However, the most valuable scientific information that could be provided by a probe is almost always how and how fast the protein functions. Development of specific proteins as detectors for specific molecules

would be a major breakthrough. Possibilities are a RuBisCO analyzer or probes to track cycle enzymes involved with the nitrogen, sulfur and other elemental cycles. The ability to measure concentrations biologically important molecules and in situ rates of various elemental cycle enzymes would constitute a major breakthrough. In situ methods to identify specific carbohydrates, the major biological exchange pool in the ocean, do not exist, but would be very useful. Specific enzyme-molecular bioprobes for chitinase/chitin, pectinase/pectin, cellulose/-ase, lectin/-ase, etc. would allow in situ tracking of rates of production and destruction of these major biochemicals in the ocean.

Sample pretreatment and concentration methods need to be developed, possibly including in situ filtration, extraction, and bubble concentration.

New, robust, low cost sensors are necessary to meet the goals of ORION and IOOS. High frequency measurements over long term deployments on cabled and uncabeled observatories require that special sensor requirements be met. This workshop detailed those requirements and attempted to visualize what the the next generation of sensors in the ocean might look like.

Workshop Recommendations
Cross cutting issues and recommendations
1. Sensor calibration must be established to ensure data quality. Self-calibration procedures are necessary, especially for autonomous sensors on extended deployments.

2. Integration of multiple sensors i.e., sensor fusion is required to address specific science questions and/or to reduce engineering requirements or instrument complexity (e.g., sensors requiring pumped sampling could be integrated).

3. Use microfabrication technologies to improve sensor integration, reduce power consumption, size, and cost.

4. Modularity and plug and play standards for communications and power must be in place for ease of sensor integration, substitution, and platform compatibility. Ethernet 10/100/1000 Base T and TCP/IP and FTP protocols are considered standard today and should be used consistently within observatories.

5. Take advantage of enhanced computing power of embedded Digital Signal Processors (DSP) and Field Programmable Gate Arrays (FPGA) for signal processing to maximize signal to noise ratio and minimize signal bandwidth for telemetry, the so called “smart sensor”.

6. Simplify and accelerate transitioning of research tools into operational oceanography. Enhanced funding opportunities are necessary to allow more rapid transition of sensors from prototype to the user community. Encourage small business investment in sensor development.

7. Sensor fouling and calibration. Fouling occurs at multiple scales and from multiple sources. Biological growth (bacterial film to invertebrate settlement) can be inhibited using toxic substances or inappropriate surface characteristics. Chemical and electrochemical corrosion can be slowed by attention to materials, surface coatings, and removal of stray electrical current. Although viewed as being unglamorous, research on biofouling is essential if long term instrument deployments will be successful.

8. Funding needs to be made available for engineers to consider MEMS, microfluidics, and other approaches to miniaturization and, ultimately, cost reduction for individual and integrated sensor systems.

9. Funding agencies should enhance their programs in ocean sensor engineering with the objective of quickly bringing ideas to commercialization. This includes extending the duration of projects so that instruments may be developed and fully tested within a single project.

10. The research community needs to establish centers that would address the following issues:

a. Act as a clearing house for information on sensor development to provide critical data on what is available, what is in development and pros and cons of specific directions in sensor development. Provide a failure-reporting system modeled after that of the National Transportation Safety Board.
b. Provide standardization of communications, power, and physical connections
c. Provide both laboratory and field based facilities for calibration, maintenance and training in use of specific sensors/instruments through community-wide workshops.
d. Evaluate sensors/instruments for sufficient robustness for operation in remote, harsh environments (e.g., deep-sea, high latitudes, etc).
e. Certification of instruments and other standards (e.g., an Underwriter Laboratory for oceanographic sensors
f. Provide the infrastructure for educating the next generation of engineers and technologists in sensor design and operation (micro mechanics, electronics, fluidics, physics, chemistry, acoustics, optics, and seagoing technologies).

Specific recommendations from each working group

Population density and community structure
Techniques are needed for automated species-level identification using molecular probes combined with optical imaging and acoustic systems to cover appropriate scales. Although some technologies have been identified and tested on the lab bench, new approaches to sample collection, processing, and analysis of specific biochemical compounds need to be developed.

New methods are needed to:
1. Combine acoustics to sample 10s of meters to m scale, optics to sample m to um scale and discrete samples for analysis of genes and gene products (DNA, rRNA, mRNA).
2. Fuse multiple sensors into instruments designed to address specific questions is considered a priority.
3. Collect and process biochemical samples

Techniques to be accelerated:
1. fiber optic-based, capillary waveguide biosensor technology
2. Nucleic Acid Sequence Based Amplification
3. in situ hybridization techniques
4. multi-frequency acoustics (backscattering)
5. low frequency acoustic tomography (absorption)
6. high resolution optics to sample multiple particle materials and spatial scales synoptically
7. LIDAR
8. Holography
9. in situ methods for ion exchange, surface recognition and molecular imprinting, carbon nano-tube concentrators and selective adsorbent nano-materials

Organism Behavior
A major challenge is to increase sample volume while continuing to quantify the environment on scales of animals within a 1 m^3 volume.

New methods are needed to:
1. Increase sample volume, resolution, and sensitivity.
2. Detect change in the organisms' chemical environment
3. Develop robotic organisms on appropriate scales using nano-technology (e.g., The Nanopod, a robotic copepod used to test ideas about copepod behavior).

Techniques to be accelerated:
1. Laser based LIDAR detectors and imaging systems
2. multispectral optics
3. low frequency acoustic absorption
4. RAMAN spectroscopy
5. LIBS
6. combine optics and acoustics (e.g., FishTV, Biomaper II)
7. nano-technology in robotics

Processes occurring at the air/water interface
In situ gas sensors that currently exist are too slow and unable make in situ measurements on the rapid time and space scales required to measure gas flux.

New methods are needed to measure:
1. In situ gas concentrations on smaller spatial scales (10 um) and at shorter response times (100 Hz for CO2, for example)

2. Methane, hydrogen, hydrogen sulfide, radon, the inert gases argon, neon, and helium; C2-C4 hydrocarbons, the nitrogen oxides, halocarbons including Freon, bromine, mercury, sulfur gases, and sulfur hexafluoride, which is used to track the distribution of chemical and biological species by tracer release experiments.

Techniques to be accelerated
1. NDIR
2. Long pathlength absorbance spectrometry
3. Organic Light Emitting Diodes as used in multi-analyate sensors
4. Gas voltammetry
5. ISFETs solid state electrodes
6. fiber optic based optodes
7. RAMAN spectroscopy

Processes occurring at Vents and seeps
Limitations of existing sensors are their inability to follow the rapid chemical and biological changes in both cold seeps and hydrothermal vent environments over long periods of time.

New methods are needed to:
1. Operate in harsh chemical environments and at interfaces between fluids and mineral surfaces
2. Initiate event-triggered sampling whereby measurements commence with the start of unusual seismic activity, or anomalous changes in vent fluid or seep chemistry, as monitored by some robust continuous monitoring device.

Techniques to be accelerated:
1. voltammetry
2. UV-Visible spectroscopy
3. LIBS
4. RAMAN spectroscopy

Biogeochemical processes occurring in the water column
There is a critical need for adaptive event driven sampling and for in situ sensors to track and monitor processes in difficult environments which cannot be studied in other ways.

New methods are needed to measure:
1. Photosynthesis (primary production), O_2, pCO_2, and pH at high spatial and temporal resolutions
2. Anoxia events and coupled sulfur compounds.
3. Small amounts of chemicals which affect biological reproduction and mating.
4. The *in situ* sinking speeds and flux rates of organic and inorganic particles which bring nutrients and energy to the deep-sea.
5. Macro and micro nutrients, O_2, pH, CO_2, metals, H_2S, and biological parameters at 1% accuracy, 1 % precision per second, N_2O and metals.

6. Specific proteins as detectors for certain molecules such as a RuBisCO analyzer or probes to track cell cycle enzymes involved with the nitrogen, sulfur and other elemental cycles

Techniques to be accelerated:
1. FFRP-like sensors to measure photosynthetic rate
2. voltammetry
3. UV-Visible spectroscopy
4. non-destructive optical imaging of cellular and particulate fluorescent activity
5. non-destructive optical imaging of birefringence (crystalline) characteristics of particulates and plankton (e.g., marine snow, coccolithophores, invertebrates)
6. fiber optic time domain array processing of chemical identities
7. in situ hybridization using DNA/DNA, RNA/DNA approaches
8. RAMAN spectroscopy for organics

Processes occurring at the sediment/water interface
Very little is currently known about fluid migration from bottom sediments into the ocean bottom waters from any process other than diffusion.

New methods are needed to measure:
1. Chemical characterization (finger printing) of intractable organic matter (DOC, kerogen, etc).
2. Radon for long-term seep monitoring
3. Chemical/physical characteristics of particles simultaneously over time.
4. Specific organic compounds related to redox zones and microorganism community

Techniques to be accelerated
1. Voltammetry
2. UV-Visible spectroscopy
3. RAMAN spectroscopy
4. LIBS
5. in situ mass spectroscopy
6. miniturazed HPLC through microfluidics