Marine Chemical Technology and Sensors for Marine Waters: Potentials and Limits

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Abstract

A significant need exists for in situ sensors that can measure chemical species involved in the major processes of primary production (photosynthesis and chemosynthesis) and respiration. Some key chemical species are O_2, nutrients (N and P), micronutrients (metals), pCO_2, dissolved inorganic carbon (DIC), pH, and sulfide. Sensors need to have excellent detection limits, precision, selectivity, response time, a large dynamic concentration range, low power consumption, robustness, and less variation of instrument response with temperature and pressure, as well as be free from fouling problems (biological, physical, and chemical). Here we review the principles of operation of most sensors used in marine waters. We also show that some sensors can be used in several different oceanic environments to detect the target chemical species, whereas others are useful in only one environment because of various limitations. Several sensors can be used truly in situ, whereas many others involve water brought into a flow cell via tubing to the analyzer in the environment or aboard ship. Multi-element sensors that measure many chemical species in the same water mass should be targeted for further development.

INTRODUCTION

Over the past decade, several reviews have discussed specific individual chemical and/or biological sensors needed for ocean observatories with a primary focus on upper ocean processes (e.g., Daly et al. 2004, Johnson et al. 2007a, Prien 2007). Real-time information from sensors that can be deployed for long periods without (bio)fouling will revolutionize our understanding of ocean processes much as improved telescopes and satellite packages have enhanced our knowledge of the solar system and beyond. To this end, the National Science Foundation is planning the implementation of the Ocean Observatories Initiative (OOI), which seeks to further develop the science and technology needed to establish fixed ocean observing systems capable of continuous data collection. Reliable and portable sensors are also needed for mobile assets that include gliders, drifters, autonomous underwater vehicles (AUVs), human occupied vehicles (HOVs), remotely operated vehicles (ROVs), and autonomous buoys, as well as on ships with conductivity, temperature, depth (CTD) packages, profilers, inline systems, and pump profilers.

In this review, we discuss chemical sensors that can be used to study processes that occur in the ocean, including suboxic/anoxic stratified basins and hydrothermal vents. The chemistry described is driven by physical events such as storms and tides and, more importantly, the biogeochemical processes of primary production (both photosynthesis and chemosynthesis) and secondary production (respiration) using O_2 and alternate electron acceptors (NO_3^-, MnO_2, FeOOH, SO_4^{2-}). In addition to O_2 measurements, the detection and quantification of pCO_2, dissolved inorganic carbon (DIC), pH, nutrients (including N_2 for N fixation), H_2S, and trace metal micronutrients are essential to better understand spatial and temporal fluctuations in primary productivity. Additionally, the formation of volatile organic compounds (VOCs) in the water column has direct bearing on atmospheric processes. Important secondary processes include but are not limited to pollution, ocean acidification, $CaCO_3$ dissolution, annamox, methane oxidation, and metal oxidation and precipitation. As Brandes et al. (2007) pointed out in a recent review, the marine N budget is still not well known and other element cycles are not fully appreciated. To better constrain element budgets, more components of each element cycle must be measured more frequently and with better spatial/vertical resolution. A detection limit (DL) of nanomolar or lower for some analytes and a precision of better than 0.2% for analytes that are found in significant concentrations are necessary. Versatile sensors of analytes of interest that are functional in a variety of environments including extreme ones are highly desirable.

We describe the performance of single-analyte sensors both alone or coupled with other sensors. However, we realize that several single-analyte sensors within a single package often do not necessarily measure the same water mass depending on environmental conditions. Multianalyte sensors that can measure several chemical species simultaneously on the same water mass are clearly preferred. This simultaneous measurement is critical for systems with large redox or chemical gradients over short distances, such as sediments and stratified basins, and within dynamic systems that change rapidly over short time periods, such as hydrothermal vent waters emanating from chimneys and diffuse flow sources. Having information on both an oxidant and a reductant (any two or more reactants or products of a reaction) in the same time and space will allow researchers to more fully describe chemically and/or microbially driven processes.

Ideally, an in situ device directly measures a chemical species in the environment without extracting or isolating a sample from its natural surroundings. However, this ideal situation is often not possible owing to fragile instrument components or specific conditions required for analysis. Therefore, the use of a membrane or pump to bring samples to the sensing element for analysis is also considered in situ. The pump can be in close proximity to the sample or the sample can be pumped from depth to an analyzer aboard ship. It is imperative that the sample does not come

in contact with the atmosphere, another water mass, or undergo any chemical change in transit to the sensor (e.g., precipitation of a metal sulfide species as hydrothermal vent water is cooled to ambient ocean temperature). Frequently this requirement can be addressed by independent measurements with a direct sensor at the pump inlet for one of the reactive analytes measured.

In addition to uncertainties associated with changing chemical compositions, coupling a sensor to a pump or membrane can significantly impede instrument response time. The sensor may or may not require the use of reagents to convert the target analyte into another compound that can then be detected. Typically, sensors that require reagents to be mixed for final analyte detection have longer response times and require holding tanks for spent materials to prevent pollution in the environment under study; thus reagentless sensors are preferred.

Some sensors have significant power and space requirements and are more useful on a package lowered or powered from a ship, ROV, or HOV. Longer deployments are possible if these sensors are on a cabled observatory that could provide nearly unlimited power and bandwidth for communication. Other sensors with lower power requirements can be used on a tether or moorings with limited power from wind or solar sources. The extent to which power requirements and communication systems/data storage should be weighed depends on a study's intended timescale and deployment area. Additionally, factors such as (bio)fouling should also be considered.

We discuss recent advances in chemical sensors and elaborate on multielement sensors and the types of environments that were not previously given significant attention. Throughout we attempt to identify the potential and limits of in situ marine chemical sensors by placing emphasis on temporal and spatial resolution. The latter includes vertical resolution in both sediments and stratified water columns. In addition to DLs and precision, we discuss selectivity, response time, power requirements, overall robustness, and the effect of varying physical factors (temperature and pressure) on instrument response. Marine sediments are not discussed here, because they are beyond the scope of this review, and recent reviews by Reimers (2007), Viollier & Rabouille (2003), and Boudreau & Jørgensen (2001) describe this system. Processes that occur within marine sediments are similar in nature to those that occur within the water column; however, sensors used in sediments face the additional challenge of being able to function in sediment without disturbing it.

ANALYTICAL TECHNIQUES

Recently a number of analytical techniques have been adapted for in situ applications, enabling far greater spatial and temporal resolution relative to conventional methods. The first truly in situ chemical measurement was performed for salinity in 1961 (Brown & Hamon 1961), which began the modern age of oceanography (Wangersky 2005), and during this time period the first autonomous (self-reporting) buoy was proposed. Today it is possible to measure a broad range of analytes quickly and accurately using a number of different techniques and in some instances with the same technique. Below are the major classes of analytical tools currently available for in situ chemical measurements, some of which have been reviewed (Daly et al. 2004, Johnson et al. 2007a, Prien 2007). Lists of commercially available and independently tested instruments are available through the Alliance for Coastal Technology (**http://www.act-us.info/**). We briefly review the principles of operation of the common sensors used in marine waters.

Electrochemical Techniques

Electrochemical sensors are among the most widely used in situ chemical sensors today. Electrochemical sensors or electrode systems include conductivity (salinity) (**Table 1**), potentiometry (e.g., glass pH electrode), amperometry (e.g., Clark-style O_2 electrode), and voltammetry. Reviews

Table 1 Current techniques for in situ measurements of dissolved gases, pH, nutrients, and micronutrients[a]

Analyte	Detection limit	Response time	Environmental types[b]	Deployment type[c]	Lifetime	Comments	Key references
Electrochemistry—Single Analyte							
O_2, cathode-type amperometric	0.1 μM				>1 year	Drift during use; H_2S, Mg^{2+}, Ca^{2+} interference; O_2 consumption; difficulties with flow and diffusivity	Baumgartl & Lubeers 1973, Whalen et al. 1967
pO_2, Clark-type amperometric	0.1 μM	0.1 s	I-III	1–6	Months to >1 year	Low change from stirring/diffusivity; H_2S interference	Atkinson et al. 1995, Revsbech 1989, Revsbech & Ward 1983
N_2O/O_2 cathode-type	0.1 μM	1.5–12 s	I,III		1 week	H_2S interference; sensitivity varies with sensor, age of sensor, tip size, and stirring	Revsbech et al. 1988
NO_x^- biosensors	<1–5 μM	s to min	I,III		<3 months	Insensitive to stirring, pH, and O_2; responds to any NO_2^- and N_2O in system; temperature (12°C to 20°C) and capacity of denitrifiers affect linear range	Larsen et al. 1996, 1997; Meyer et al. 2001; Nielsen et al. 2004
NO_2^-, ISE	10 μM	10–15 s	I,III		Days	Cl^-, H_2S, and sulfite interference	de Beer et al. 1997b
H_2S	1 μM	<100 ms	III			Low stirring sensitivity; interference due to O_2, SO_2, and intense ambient light	Jeroschewski et al. 1996, Kuhl et al. 1998, Pringault et al. 1999, Wieland & Kuhl 2000
H_2S, YSZ ceramic ISE	—	min	IV	5	Days	Works from 125°C to 400°C and up to 4000 m	Ding et al. 2001

CO_2 ISE	<3 μM	10 s	I,III		Weeks	Interference from acid gases and H_2S; works from 10°C to 50°C	de Beer et al. 1997a, Zhao & Cai 1997
pH, glass ISE	1–14	15 s	I-IV	2–6	Months to year	Works from 0°C to 120°C and up to 3000 m; precision ± 0.06	Amman 1986, Le Bris et al. 2001, Thomas 1978
pH, YSZ ceramic ISE	3–9	<5 min	IV	5	Days	Works from 10°C to 400°C and up to 4000 m with a precision ± 0.03	Ding & Seyfried 2007
pH_2	0.1 mM	<5 min	IV	5	Days	Works at 125°C to 400°C and up to 4000 m	Ding & Seyfried 2007
Electrochemistry—Multi-Analyte (Voltammetry)							
O_2, S_{Tot}, Fe^{2+}, Mn^{2+}, $S_2O_3^{2-}$, $S_4O_6^{2-}$, I^-, FeS, soluble organic Fe(III)	μM	1–10 s	I-IV	1–6	Several months	In situ conditioning (self-cleaning); works from 1.5°C to 100°C and up to 3000 m	Brendel & Luther 1995, Luther et al. 2008, Taillefert et al. 2000, Theberge & Luther 1997
GIME array [Cu(II), Pb(II), Cd(II), Zn(II)]	nM	nM	III	2,6		No influence from sample matrix; O_2 interference when in an unbuffered environment; applicable at depths <100 m	Tercier-Waeber et al. 2000
Optodes							
O_2	7 μM	s to min	I-IV	1–6	Year	Ease of use, long-term stability	Kraker et al. 2008, Liebsch et al. 2000, Martini et al. 2007, Tengberg et al. 2006
pH	4–9	s to min	1-IV	1–6		Temperature and salinity effects; most commonly used in chamber studies	Gao et al. 2007, Kraker et al. 2008, Schroeder et al. 2007b, Stahl et al. 2006

(*Continued*)

Table 1 (*Continued*)

Analyte	Detection limit	Response time	Environmental types[b]	Deployment type[c]	Lifetime	Comments	Key references
pCO_2	2.5 mbar	min	I-III	1–6			Liebsch et al. 2000, Schroeder et al. 2007a
H_2S	0–25 μbar	s–min				Has been tested only in the lab	Choi & Hawkins 2003
UV-Vis Spectroscopy							
NO_3^-, HS^- (ISUS)	0.2–1.5 μM	s	I-III	1–6	Months to year	High spectral and spatial resolution; low temperatures bias NO_3^- concentrations; works at depths <1000 m	Johnson & Coletti 2002
NO_3^-, NO_2^-	0.9 μM		I,III	2–3,6	Months	High spectral resolution by deconvolution	Sandford et al. 2007
NO_3^- (SUV-6)	0.2 μM	s	I,III	2		Precision >0.21 μM; works up to 5000 m	Finch et al. 1998
Colorimetry							
NO_3^-, NO_2^-, PO_4^{3-}, NH_4^+, silicate, TN, TP	nM	several min	I,III	1–6	Weeks to months	Reagent degradation and consumption determine length of deployment	Adornato et al. 2007, Daly et al. 2004
Fe (II,III)	0.1 μM	15 min	I-IV	4–6	Months	Reagents must be replenished	Chapin et al. 2002, Sarradin et al. 2005
pCO_2	1 μbar	45 s	I,III	1–6	Several months	Must be modified to operate at depth; operation depths <100 m	DeGrandpre et al. 1995
pH	1–14	10 s	I,III	2,6		Operation depths <1000 m; precision ±0.001	Nakano et al. 2006, Wang et al. 2007
S_{Tot}, O_2, $Si(OH)_4$, NO_3^-	μM	s–min	IV	5		Works from 5°C to 25°C ~3000 m; high resolution	Johnson et al. 1986, Le Bris et al. 2000

IR Spectroscopy							
VOCs	ppb	5–10 min	I,III	1–5		High power demand; detection limits are insufficient for background analysis of less abundant VOCs; works from 3°C to 20°C and up to 300 m	Kraft et al. 2003
Raman Spectroscopy							
O_2, N_2, CO_2, CH_4	dbar	s	I-IV	1–5		High power demand; low sensitivity; works from 0°C to 200°C and up to 4000 m	Brewer et al. 2004
SO_4^{2-}, CO_3^{2-}, NO_3^-	mM to μM	s	I-IV	1–5		Low sensitivity; works from 0°C to 200°C and up to 4000 m	Pasteris et al. 2004
MIMS							
O_2, N_2, Ar, CO_2, CH_4	ppm	s–min	I,III	1–5		Temperature and pressure effects; applicable up to 500 m	Bell et al. 2007, Camilli & Hemond 2004, Kibelka et al. 2004, Lloyd et al. 1996, Wenner et al. 2004
VOCs (chloroform, toluene, DMS, benzene, trichloroethane)	ppb	s	I,III	1–5		Inlet clogging; time lag between sample acquisition and analysis	Kibelka et al. 2004, Short et al. 2001, Short et al. 1999, Short et al. 2006, Wenner et al. 2004

[a]Representative marine chemical sensors currently used in situ. This table is not an exhaustive list of all chemical sensors or associated references. Abbreviations: ISE, ion selective electrodes; YSZ, Yttria-stabilized zirconia; ISUS, in situ UV analyzer; VOCs, volatile organic compounds; DMS, dimethyl sulfide; GIME, gel-integrated microelectrode.

[b] Environmental types identify where a particular sensor has been or could potentially be used. Numerals (I-IV) correspond to the (I) surface ocean, (II) deep ocean, (III) coastal waters, and (IV) hydrothermal vents.

[c]Deployment types (1–6) identify the capability of a particular sensor to be used on a (1) pump profiler, (2) conductivity, temperature, depth (CTD)/rosette, (3) towed platform, (4) cabled observatory, (5) remotely operated vehicle (ROV)/human occupied vehicle (HOV)/autonomous underwater vehicle (AUV), and (6) autonomous buoy.

of these techniques include those by Luther et al. (2008), Tercier-Waeber & Taillefert (2008), Taillefert et al. (2000), Hanrahan et al. (2004), and Winkler et al. (2004). Conductivity is well known and not discussed.

Potentiometry (pH)/ion selective electrodes. Ion selective electrodes (ISEs) have the capability of measuring (sub)nanomolar levels of a target analyte (e.g., Bakker & Pretsch 2007, De Marco et al. 2007). In potentiometry, the difference in potential (ΔE) between a reference and working electrode separated by a membrane (e.g., glass for pH) is related to the concentration of a specific ion of interest. A key for long-term deployments is the stability of the reference electrode, which must not be allowed to have current pass through it or the ΔE will vary and affect the resulting concentration reading. For cations and anions, many sensors are available. The key is the selectivity of the target analyte in a highly saline environment (Bakker & Pretsch 2007). The Na^+ and Cl^- concentrations of seawater generally prevent ISEs for some cations (NH_4^+) and anions (NO_3^-) from being reliable sensors at the concentrations (μM to nM) needed. Thus, significant improvements in selectivity are needed.

Amperometric sensors. Amperometry measures the current at a given applied potential between a working and a reference electrode (Taillefert & Rozan 2002). Typically this technique has been used to measure O_2 with the Clark sensor, which has a membrane to allow O_2 to pass to the electrodes and thus prevent other interfering analytes from being measured.

Voltammetry. Voltammetry uses three electrodes (working, counter, and reference). A potential is applied between the working and reference electrodes as the current is measured between the counter and working electrodes (Taillefert & Rozan 2002, Rajeshwar & Ibanez 1997). Both current and applied potential are measured, and the relationship is plotted in the resulting voltammogram (current versus applied potential). Voltammetry is the most versatile of the electrochemical techniques because it is able to measure the concentration (via the current) of several species (indicated by the specific applied potential at which a given electrode reaction generates current) in a single electrochemical experiment or "scan." Any metal can be used as a working electrode but Hg or Hg films are used most often.

Optical Methods

To date, UV-visible light (UV-Vis), optodes, infrared (IR), and Raman spectroscopy have been used to measure a variety of analytes, including dissolved gases, nutrients, and trace metals (**Table 1**). Although UV-Vis spectroscopy thus far has been the most versatile for detecting single or multiple analytes, this technique is most commonly used as a single analyte method unless coupled to flow injection analyzers (FIA) or autoanalyzers. The different optical techniques are described below.

A major advance in detecting (sub)nanomolar levels of nutrients and metals has been facilitated by the use of a long pathlength liquid-core waveguide (LCW; also known as a liquid-waveguide-capillary cell). LCWs operate by confining light within the waveguide by using a material with a refractive index less than that of water (Byrne & Kaltenbacher 2001). By confining light within a waveguide, long cell pathlengths can be obtained (>4 m). The theory and application of LCWs has been reviewed by Dallas & Dasgupta (2004) and Gimbert & Worsfold (2007). This technology is readily applicable for use with FIAs.

UV-visible spectroscopy. Most nutrient analyzers (N, P, Si) measure the absorbance of UV-Vis light after reaction of the analyte with a reagent specific to the species of interest. The product

of this reaction absorbs light at a known wavelength where there is no interference from other absorbing species in the system. When the absorbance at only a single wavelength is measured, this method is termed colorimetry and is based on well-known methods that have been applied to nutrients, sulfide, and metal analyses (Grasshoff et al. 1983, Parsons et al. 1984). Because colorimetry requires the treatment of the sample with a reagent, specialized sample introduction (such as FIA) is required so that a sample can be drawn into the system for reaction. Because a reagent must be supplied and waste is produced in the process, these methods have limited applicability to long-term deployments.

The in situ UV spectrophotometer (ISUS; Johnson & Coletti 2002) is the only UV multi-analyte analyzer presently available. The ISUS functions only in the UV region by using a diode array detection system, which is capable of simultaneously measuring absorbance over a range of wavelengths. The ISUS measures the absorbance of UV light by NO_3^-, NO_2^-, Br^-, I^-, and HS^-, each of which absorbs UV light at a unique wavelength. This sensor has a fast response time (seconds). Although the sensor is susceptible to biofouling, it has operated for more than three months without sensor degradation in estuarine environments (Johnson & Coletti 2002).

Optodes. Optodes (or optrodes) are optical sensors that use indicator dyes mounted in a matrix or polymer layer. Optodes are commonly used to measure oxygen on a variety of platforms, and are also used to measure pH and pCO_2 (**Table 1**). Fluorescence is excited by a light-emitting diode (LED) or other light source, and then fluorescence (light emission) measurements are made by monitoring the changes in either light emission, lifetime of the decay signal, or ratiometric observations (Amao 2003, Basabe-Desmonts et al. 2007). Fluorescence intensity measurements suffer from fluctuations in light source intensity, photobleaching, drifts in the optoelectric setup, and background fluorescence (Gao et al. 2007). Light decay or (lifetime-based) measurement techniques are more reliable than fluorescence intensity measurements because the fluorescent lifetime is not affected by the factors that limit intensity measurements, but sophisticated and expensive equipment is required. Ratiometric techniques use either indicators sensitive to a reagent at two different wavelengths or the combination of a nonreactive reference dye and an indicator dye (Gao et al. 2007).

Most optode measurements have focused on single-analyte techniques. Recent lab-based studies using time domain dual lifetime referencing (td-DLR) have simultaneously measured pH or pCO_2 and pO_2 (Schroeder et al. 2007a,b). pH is particularly sensitive to temperature and ionic strength. Kraker et al. (2008) used a polarized organic LED light source and a polarized organic photodiode to block excitation light but permit emitted light to the detector to simultaneously monitor O_2 and pH. This latter technique is limited to flow-through devices owing to the need for two polarization filters.

Infrared spectroscopy. IR methods in the marine environment use the spectral range from 4000–400 cm^{-1} (Kraft et al. 2003). IR may be used to study the fundamental vibrations of molecules to identify and quantify a variety of compounds simultaneously. IR active peaks are strongest for molecules that have a dipole moment, and many organic compounds are susceptible to measurement. Therefore, IR has advantages for both selectivity and sensitivity (Holst & Mizaikoff 2002); however, normal DLs approach only (sub)micromolar levels.

Transmission and attenuated total reflection (ATR) are employed in IR spectroscopy. Transmission methods are not optimized for working in aqueous solutions. Owing to a broad and strong water absorption band, the possible transmission path length cannot exceed a few micrometers, resulting in limited sensitivity (Kraft et al. 2003). Therefore, only ATR transducers have been applied to the marine environment. ATR uses a property of total internal reflection to generate

an evanescent wave. A beam of infrared light is passed through the ATR crystal so that it reflects at least once off of the internal surface in contact with the sample. This reflection forms the evanescent wave that extends a few micrometers into the sample. Any IR-absorbing molecule in the evanescent penetration depth layer will absorb energy from the field at specific wavelengths.

Kraft et al. (2003) reported the use of an in situ Fourier Transform IR (FT-IR) system mounted on a ROV that utilizes a polymer-coated ATR cell and silver halide (AgX) optic fibers. For detection of trace analytes, the ATR cell surface was coated with a membrane that selectively enriches the target analytes while excluding water. A hydrophobic polymer layer (propylene/ethylene copolymer) with a thickness greater than the penetration depth of the evanescent field was added to the fibers because AgX can be corroded by chloride ions. The hydrophobic polymer film helps prevent biofouling and increases sensitivity via preconcentration (Kraft et al. 2003). However, the use of a film results in slow response times (minutes). There is no salinity or turbidity effect, but the system can operate only down to 300-m depth and within a 3–20°C temperature range (Kraft et al. 2003).

Raman spectroscopy. Raman spectra are acquired by irradiating samples with a powerful laser source of monochromatic light in the visible region. If a molecule is Raman active, the target will scatter a small fraction of the radiation, shifting the wavelength of the incident beam depending upon the chemical structure of the target. The shift in wavelength is similar in energy to that in IR spectroscopy, described above. Raman active peaks are strongest for molecules that are symmetrical and do not have a dipole moment, e.g., homonuclear diatomic molecules, CH_4, CO_2, and SO_4^{2-}. Thus, Raman spectroscopy can work in water better than IR methods do. The use of a laser makes Raman analyzers resistant to biofouling; however, these instruments are currently large and have a high power demand, making them unsuitable for autonomous studies over long periods of time. To be useful in a broader range of applications DLs will need to be improved for most analytes.

Mass Spectrometry

Mass spectrometry is an invaluable tool in analytical chemistry, providing elemental, structural, and isotopic information on a range of environmental species from small, simple molecules to large biomolecules (Richardson 2001). In mass spectrometry, analytes are introduced to a vacuum, ionized, separated in space or time by magnetic and/or electronic field(s) according to their mass to charge ratio (m/z), and finally detected. The inherent sensitivity and nonselective nature of mass spectrometry make it the most versatile sensor available and an attractive tool for analyzing samples in situ. Traditional, lab-based mass spectrometers have been converted to shipboard use by adding a pump for sampling the water (Tortell 2005). Truly in situ mass spectrometers operate underwater and must maintain a vacuum ($<10^{-5}$ Torr) in a submersible system (Short et al. 1999), which has been accomplished using membrane-induced mass spectrometry (MIMS), a system that uses a silicone membrane to allow selective transport of nonpolar species and exclusion of polar species such as water or salts (Ketola et al. 2002). It is not yet clear how physical factors such as temperature and pressure affect the diffusion of analytes across the membrane, which makes quantification difficult (Tortell 2005). Calibration for the pressure effect on the membrane has been carried out (Bell et al. 2007), and O_2 measurements performed to a depth of 500 m agree well with external CTD and oxygen sensors. These systems are being refined to conserve power and space to make them suitable for a wider range of in situ applications. The NEREUS (novel, efficient, rapid evaluation of underwater spectra) instrument developed by Camilli & Hemond (2004) has the double-focusing characteristic of crossed magnetic and electrical fields, which

provides relatively high mass resolution for a compact mass analyzer size and minimizes power consumption. Additionally, techniques such as electrospray ionization (ESI) have been considered for incorporation into an in situ mass spectrometer to detect both polar and nonpolar species (McMurtry & Smith 2001, Short et al. 2001).

Mass spectrometry has the distinct ability to differentiate between isotopes of the same element. Presently the detection of low abundance natural isotopes (^{15}N, ^{13}C, ^{18}O, and ^{34}S) is not possible in situ, but more sensitive and higher mass resolution instruments could measure isotopic tracers, which are essential for understanding global cycling of many elements. Isotopic information could also provide more definitive data by which to identifiy a chemical species, because many analytes may have the same *m/z*. Kibelka et al. (2004) demonstrate that when resolution is high enough, MIMS has the unique ability to internally corroborate data with secondary signals and identify any potentially interfering ions.

Flow Analyzers

Almost any detection system can be coupled into a flow cell and isolated from the environment. The system can be made autonomous or can be coupled with a pump profiling system (discussed below). Flow systems have been widely used since the mid 1970s and offer a convenient method to apply laboratory wet-chemical techniques to in situ studies. Electrochemical flow cells have been described and used for direct detection without preconcentration for Fe and S species (Luther et al. 2002) and for the detection of trace metals with preconcentration by electrochemical deposition at a working electrode (Tercier-Waeber & Taillefert 2008).

Although flow analyzers are not truly in situ (because the sample is removed from the environment for analysis), they are valuable tools for measuring multiple analytes in a range of environmental settings by combining several detectors into one analytical package or autoanalyzer. Advances in microfluidics will help to advance this technique further by making instrumentation cheaper and reducing the volume of sample and reagent consumed (Gray et al. 2006, Prien 2007).

Flow injection analyzers. Gray et al. (2006) provide a detailed review of different flow injection techniques and their applications. Flow systems using light detection may require on-line sample filtration to prevent blockage of light and fouling of the cell. Flow injection analyzers and autoanalyzers are most commonly used for in situ UV-Vis and colorimetric analyses, because many laboratory-based methods (Grasshoff et al. 1983) can be readily automated. In situ calibration is important owing to sensor drift and reagent degradation over time. Changes in salinity and other changes in sample matrix can also cause changes in sensitivity and must be compensated for in situ. However, the use of additional reagents limits in situ applications for long-term monitoring owing to reagent storage and degradation and the need for waste storage.

Pump profiling. Pump profilers operate by pumping water from depth (~400 m) directly to a shipboard instrument. The pump inlet is typically located on a CTD or other profiler, allowing for the integration of other measurements commonly performed on a CTD/rosette system. Any instrument that can analyze samples with inline sample processing can be feasibly used in this fashion. FIA and multichannel autoanalyzers are particularly useful tools (Codispoti et al. 1991).

OPEN OCEAN

The open ocean (depth >200 m) covers 92% of the sea floor (Sverdrup et al. 1942) and is vital to the health of the planet even though it is not as locally productive as the coastal ocean. Remote

sensing and the deployments of drifters have provided a wealth of physical information and O_2 data concerning the open ocean (e.g., Riser & Johnson 2008). However, to fully understand the biogeochemical and abiotic processes (dust flux, air-sea gas exchange) occurring within the open ocean, we need to monitor O_2 along with nutrients (NO_3^-, PO_4^{3-}, SiO_2), micronutrients (trace metals), DIC, pCO_2, pH, and other dissolved gases (N_2, N_2O, Ar). Presently no single analytical technique or analytical package can measure all these at the necessary DLs [in some cases (sub)nanomolar] and precision (**Table 1**). Spatial resolution and response time are typically not an issue in open ocean studies, because many processes occurring in these regions are slow and broad in scale (e.g., figure 2 in Dickey 2003). One exception to this is vertical profiling, because the rate of descent of a CTD or profiler (which dictates the vertical resolution) will be limited by the response time of the slowest sensor.

Upper Ocean

Photosynthesis is limited by the depth to which light can penetrate (~100 m) and the availability of nutrients in oligotrophic regions. Photosynthesis can also be limited by micronutrients such as iron in high-nutrient, low-chlorophyll (HNLC) regions. Uptake of micronutrients leads to the biolimiting type profile found in **Figure 1**. Chemical species with this type of profile are a challenge to analyze because nanomolar or lower concentrations must be detected to characterize primary productivity and respiration. Short-lived blooms can occur by the addition of nutrients

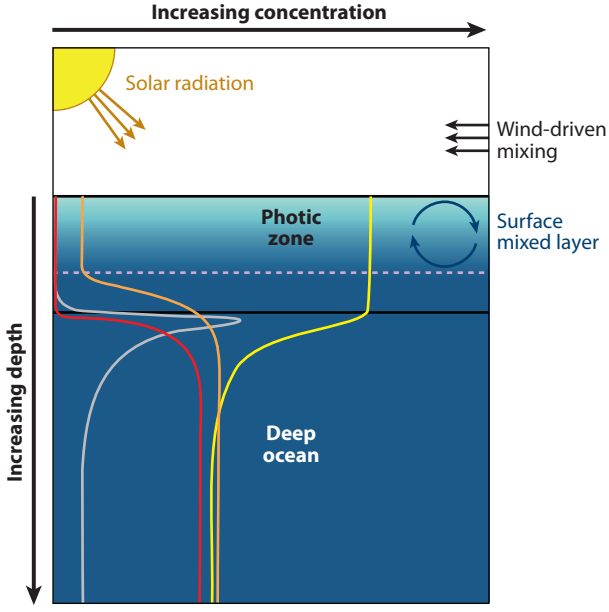

Figure 1

Generalized diagram of nutrient and dissolved gas profiles in the open ocean and the processes affecting them. Nutrients with a bio-intermediate depth profile (*orange*) are not limiting for biological growth and are regenerated at depth owing to respiration. Nutrients with a bio-limiting depth profile (*red*) are limiting for biological growth. Gases with a dissolved profile (*yellow*) are near saturation in the surface waters and can be undersaturated at depth owing to cooler temperatures, which increase gas solubility. Oxygen can be undersaturated and pCO_2 enriched owing to consumption/production during respiration. The depth profile of a short-lived intermediate (*grey*), such as NO_2^-, can be produced during respiration.

via wind-blown dust, mesoscale eddies (Emerson et al. 2002), or upwelling of nutrient-rich deep waters to the surface.

Dissolved gases and pH. Gas exchange with the atmosphere is limited to the surface mixed layer, which can range from 10 m to over 100 m (Montegut et al. 2007). Dissolved gases are involved in a number of biotic and abiotic processes within the photic zone and with profile shapes indicative of consumption, production, or conservative behavior (**Figure 1**). O_2 and the carbonate system [CO_2, DIC (carbonate alkalinity), and pH] are involved in photosynthesis, respiration, and exchange with the atmosphere so understanding their dynamics is of great importance. N_2 and other inert gas concentrations are controlled mainly by air-sea exchange processes, making them essential for quantifying abiotic processes. Trace natural gases such as N_2O, dimethyl sulfide (DMS), and CH_4 are derived from biotic sources and their measurement requires techniques with low DLs. No sensor is available for CH_4 at these DLs (Reeburgh 2007).

Oxygen. Perhaps one of the most common in situ oceanographic measurements, next to salinity and temperature, are measurements of dissolved O_2. The reliability of several sensors, especially Clark-type polarographic and pulsed polargraphic electrodes, has encouraged their routine use, but slow response times, susceptibility to fouling, and sensor drift can limit their reliability. Oxygen optodes are becoming increasingly common because they have a faster response time (dependent on membrane thickness), are stable for long periods of time, and are not affected by depth. Tengberg et al. (2006) performed a comparative study with gliders and found optodes to be highly accurate and reliable for more than 20 months. Martini et al. (2007) performed a long-term study that compared oxygen optodes with Clark-type electrodes in Massachusetts Bay, and found that both techniques gave comparable results, were susceptible to fouling, and that the Clark-type electrode consumed 17 times more power than the optode. Other techniques that can measure O_2 include voltammetric techniques using Au/Hg microelectrodes, Raman spectroscopy, and mass spectroscopy. Au/Hg microelectrodes are stable for at least two months, are resistant to biofouling (Luther et al. 2008, Moore et al. 2007), and have good DLs and precision. Raman and mass spectroscopy are also very precise multianalyte sensors that can be used to measure O_2 (**Table 1**).

Carbonate system. Thermodynamics dictates the equilibrium relationship between pCO_2, DIC, pH, and total alkalinity (A_T, assuming that A_T is not changing relative to carbonate alkalinity; Bellerby et al. 2002). pH indicates the carbonate speciation of DIC, and changes in pCO_2 will affect how much CO_2 is dissolved in seawater and how much carbonic acid is subsequently produced (higher pCO_2 will result in a lower pH). The carbonate system is directly involved in biological processes, because CO_2 is consumed during primary production and released during respiration. pCO_2 in the ocean is increasing owing to increasing concentrations of CO_2 in the atmosphere, resulting in a more acidic ocean. For example, Orr et al. (2005) report that pH in the surface ocean has already dropped by 0.1 pH units since the industrial revolution.

The carbonate system can be characterized by measuring two of the components and calculating the others. In situ measurements of the carbonate system are generally made by measuring pH and pCO_2 in situ, and then calculating DIC and A_T. pH has often been measured using potentiometric microelectrodes; however, these sensors are accurate only to ± 0.01 pH units (**Table 1**). To match the required precision of other measurements in the carbonate system as summarized by Seidel et al. (2007) ($\pm 1.5 \mu mol\ kg^{-1}$ for DIC, $\pm 2.0\ \mu mol\ kg^{-1}$ for A_T, and $\pm 1\ \mu atm$ for pCO_2), pH measurements must be accurate to 0.001 units. Spectrophotometric techniques using pH-sensitive dyes are now the most precise method for measuring pH and a number of these systems have been

adapted for in situ use with ± 0.0004 pH unit precision (e.g., Nakano et al. 2006, Seidel et al. 2007, Wang et al. 2007). This method is stable for reasonable periods of time (22 d for the Submersible Autonomous Moored Instrument or SAMI-pH) (Seidel et al. 2007) but has a slow response time (minutes).

pCO_2 is commonly measured using pH changes determined by using spectrophotometry in conjunction with a gas-permeable membrane (DeGrandpre et al. 1995; Wang et al. 2003, 2007). Additionally, MIMS is also capable of measuring pCO_2 in situ and aboard ship (Tortell 2005). DIC and A_T can be directly measured by acidifying samples (Byrne et al. 2002, Watanabe et al. 2004), which converts all the DIC to CO_2 gas. DIC is then measured in the same fashion as pCO_2, and A_T is measured by comparing the pH of the acidified sample to the predicted pH based upon the amount of acid added (the difference is equal to the change in pH due to loss of CO_2). These methods require storage of reagents and waste and so they are not as practical for long-term deployments.

N_2 and other inert gases. Inert gases are used as tracers of abiotic processes such as diffusive exchange with the atmosphere, bubble entrainment, and mixing with deep waters (Emerson et al. 2002). The solubility of gases and their rates of exchange across the air/water interface are well known, making it possible to distinguish abiotic from biological processes with high-precision gas measurements.

Emerson et al. (2002) monitored changes in pO_2 and pN_2 at the Hawaii Ocean Time series (HOT) station and found they could distinguish between physical processes (shoaling of isopycnals and/or upwelling, changes in sea surface height due to a cyclonic eddy) and biological processes, including increases in productivity due to the upwelling of nutrient-rich deep waters. These measurements were performed using a gas tension device (GTD) in conjunction with an oxygen sensor. GTDs operate by determining the total gas pressure in water. Because N_2 and O_2 are the dominant dissolved gases in the surface ocean, changes in gas tension are related to changes in saturation of these gases. pN_2 is calculated from direct O_2 and GTD measurements and is highly dependent on the reliability of the O_2 measurements made. Emerson et al. (2002) found the most significant error in the system was due to drift in the O_2 sensors. A shortcoming of GTDs is the long response time (hours), making them unsuitable for use in many applications. McNeil et al. (2006) have designed a new GTD than can operate in the surface ocean (up to 300-m depth) with a response time of 2–8 minutes. A hydrostatic response in the upper 9 m of the water column was detected in the instrument, but could be corrected. Another uncertainty in using GTD is the nonconservative nature of N_2. N_2 can be produced at depth via denitrification and can be consumed via N fixation. As with O_2, MIMS is capable of measuring multiple dissolved gases. Measuring Ar and other noble gases allows for a more robust method by which to constrain abiotic processes (Tortell 2005).

Nutrients and micronutrients. Within the photic zone of the ocean, primary productivity and other processes that depend upon it are limited by the availability of the essential nutrient or micronutrient with the lowest concentration. The major nutrients include the labile forms of N (nitrate, nitrite, ammonia, urea), P (orthophosphate and organic P-species), and Si (silicic acid) (Daly et al. 2004). Whereas present DLs for major nutrients with existing optical methods are good for HNLC regions [NO_3^-, PO_4^{3-}, and $Si(OH)_4$ concentrations greater than 1 μM], oligotrophic regions, where nM DLs are needed, present a challenge. Traditional UV-Vis techniques coupled to autoanalyzers and FIA systems have DLs ranging from the tens to hundreds of nM (**Table 1**), which is not low enough to be used in oligotrophic waters (see Daly et al. 2004, Estela & Cerda 2005, Gray et al. 2006, Patey et al. 2007, Rimmelin-Maury et al. 2007).

Detection of Fe and other micronutrients in HNLC regions is even more difficult because DLs on the scale of tens of pM are needed. At present, there is only one published method for performing in situ micronutrient analyses and that is for Mn(II), which reacts with a fluorescent reagent that can then be detected by a zero angle photon spectrometer (ZAPS; Klinkhammer 1994). Other FIA techniques for shipboard measurements (e.g., Bowie et al. 2003, 2006; Johnson et al. 2007b; Laes et al. 2005) are time and labor intensive, and will require significant refinement if they are to be used in situ. However, the use of liquid-core waveguides with FIA and colorimetric detection should be suitable for use within the oligotrophic ocean provided suspended material can be easily filtered from the sample and a suitable preconcentration method can be developed.

Voltammetric methods have the sensitivity to detect total metal content and metal speciation with inline methods aboard ship and in situ (**Table 1**). UV irradiation (power consumer) is required to break apart metal-organic complexes and make total metal measurements (Colombo et al. 1997). A gel has been used to prevent metal-complexed material and colloids from reaching the working electrode and to measure operationally defined "free" metal ions, which are most bioavailable to primary producers (Tercier et al. 1998). ISEs have also been described in lab studies for the measurement of free ions, but more work is necessary to make them usable in situ (De Marco et al. 2007).

Deep Ocean

The deep ocean extends from the bottom of the surface mixed layer/photic zone to the abyssal plain (~4000 m) with a thickness of more than 11 km in some areas. Processes occurring within these waters are dependent on inputs from elsewhere, restricting biological activity to secondary production except for chemosynthesis at environments such as hydrothermal vents (described below). Understanding the fate of organic matter in the deep ocean is key to understanding the long-term sequestration of carbon. As organic matter sinks past the photic zone it is consumed via secondary production, which leads to an increase in dissolved nutrients and pCO_2 and a potential decrease in dissolved O_2. Because the residence time of the deep ocean ranges from ~200 to 2000 years, short-term temporal studies are not an issue. However, to fully characterize the deep ocean, sensors must be able to operate at great depths and pressures. Sensors with a rapid response are preferred when profiling vertically, because the rate of descent and vertical resolution will be dictated by the slowest sensor. At present many nutrient sensors have appropriate DLs to measure nutrients at depth, but need to be made more robust to work under pressure. Biofouling will be less of an issue at depth because there is less biological activity to foul sensors as compared with the photic zone (Tengberg et al. 2006).

SUBOXIC AND ANOXIC ZONES

Environments that have O_2 concentrations <4.5 μM and H_2S concentrations <1.0 μM are called suboxic or oxygen minimum zones (Morrison et al. 1999). Those environments with no detectable oxygen and detectable H_2S are termed anoxic zones. These zones are found in highly productive waters that undergo stratification or that have physical oceanographic regimes that prevent rapid replacement of a water mass. Suboxic zones can be partially disrupted by lateral injections of different water masses (Glazer et al. 2006, Konovalov et al. 2003). Stratification is brought about by differences in densities of shallow and deep waters due to differences in temperature and salinity, and can prevent these waters from mixing. This stratification leads to chemical zonation within the water column, with steep gradients in oxidized and reduced species (**Figure 2**). Sampling across these gradients requires the ability to measure a number of analytes accurately on a fine vertical

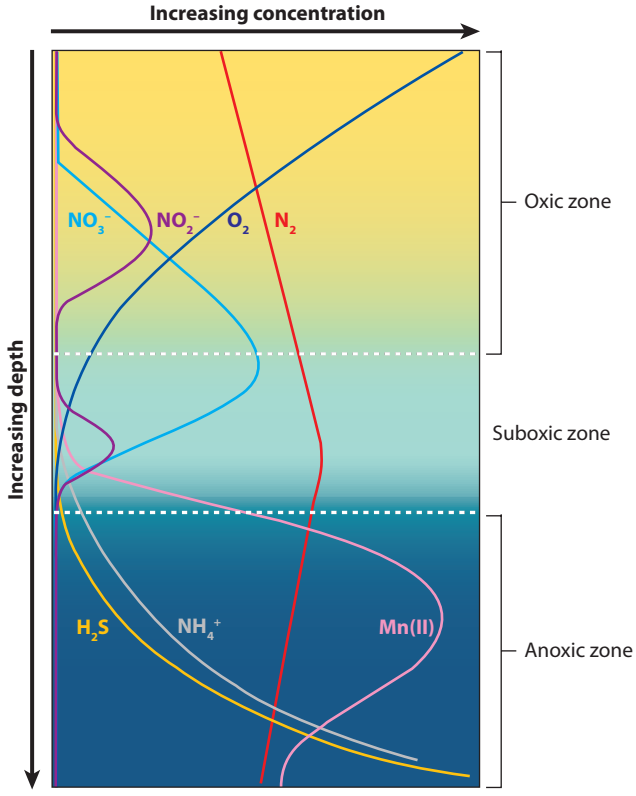

Figure 2

Generalized diagram of the suboxic and anoxic zones of the Black Sea, modified from Konovalov et al. (2006) (with permission from Elsevier) and Staley (2007). Profiles in other areas such as the Arabian Sea would be similar. However, concentrations of analytes will differ; e.g., in the Arabian Sea total dissolved Mn is <10 nM whereas in the Black Sea total dissolved Mn can be as high as 8 μM. N species can also vary significantly between systems.

profile (**Figure 2**). Many of the analytes found within these regions are highly reactive and short lived, making in situ measurements essential for understanding them.

Suboxic Zones

Suboxic zones are important biogeochemical boundaries where O_2 becomes physiologically limiting to many microorganisms during organic matter decomposition. In the absence of oxygen, NO_3^- becomes the main electron acceptor for organic matter oxidation and is lost as N_2 via denitrification, annamox, and other processes (**Figure 2**). The upper and lower interfaces of this zone are important in the cycling of a number of species including NO_2^-, NH_4, N_2O, I^-, Fe, and Mn. These areas are enriched in N species compared with the surface ocean. At the onset of these zones, NO_3^- is high in concentration from remineralization, but undergoes a decrease throughout the zone owing to NO_3^- reduction to NO_2^-, N_2O, and N_2. **Figure 2** shows representative profiles for a suboxic zone system. As a chemical species decreases, it is critical to have sensors that have excellent DLs. The analytical needs for suboxic zones are similar to those found in the upper oligotrophic and deep ocean; i.e., (sub)nanomolar DLs and operation under pressure are required.

The major requirement for describing the chemical processes occuring with suboxic zones are lower DLs; ideal DLs are in the nM range. N. Revsbech (personal communication) has shown that a Double Clark sensor (one sensor reduces the O_2 in the filling solution of the other to reduce background currents) can achieve close to 10 nanomolar DL whereas Clement et al. (2008) have shown that cyclic voltammetry at a Hg drop electrode inline to a pump profiler can achieve a 100-nM DL. Biofouling will be less of an issue in suboxic zones because O_2 is limiting for many organisms that foul sensors in the photic zone. Vertical resolution (meter) is important in examining suboxic zones because chemical concentrations and speciation can change rapidly at the oxic and anoxic interfaces and over short distances.

Anoxic Zones

Anoxia may occur depending on stratification of the water column, organic matter and nutrient loading, and topography of the basin. Permanent anoxic zones exist in parts of the world ocean (e.g., Cariaco trench) and in semi-enclosed marine environments (Black Sea and Framvaren Fjord). Seasonal anoxic zones occur in estuaries and inland bays/seas (e.g., Chesapeake Bay and the Baltic Sea). The depths of anoxic zones can be meters (inland bays and estuaries) to >1000 m for permanent anoxic basins (Black Sea and Cariaco). In these zones, H_2S and NH_4^+ concentrations approach or exceed mM levels, so sensor DLs are not a problem for those species, but other sensors need to be stable to H_2S and NH_4^+ as interferents as well as to sulfide corrosion.

At the onset of the anoxic zone, S intermediates such as FeS, S(0), $S_2O_3^{2-}$, and S_x^{2-} exist at (sub)micromolar levels. Measurement of S species can provide valuable information on whether the oxidation of sulfide is abiotic or biotic. Reduced metal concentrations increase at the onset of the anoxic zone owing to reduction of particulate metal oxides. The metals decrease within anoxic zones as metal sulfide solids are formed. Thus, methods that can measure S intermediates and reduced metals at (sub)nanomolar levels but not be fouled by sulfide are essential.

COASTAL WATERS

Coastal waters represent a small fraction of the total ocean, but are responsible for the majority of global primary production owing to elevated nutrient concentrations. High nutrient inputs in coastal waters from anthropogenic sources have lead to widespread eutrophication and overall degradation of coastal environments. Nutrient pollution is considered one of the largest global pollution problems and has led to widespread water quality issues including seasonal anoxia and an increase in harmful algal blooms (e.g., Glibert et al. 2005).

Chemically, the processes occurring within coastal waters are similar to those described above for the open ocean and suboxic/anoxic regions. Present sensors for nutrients and micronutrients have appropriate DLs in most cases. Challenges to sensor technology in these regions come from the need for high vertical resolution and the continuous monitoring of short- and long-lived events (daily, storm, tidal, and seasonal). Biofouling is a major challenge (within the coastal region) owing to the high rates of productivity and the high levels of particulate matter. Physical fouling can also be significant owing to sediment interferences with sensors (e.g., Martini et al. 2007). However, coastal regions are readily accessible to vessels of all sizes, making it possible to perform a large number of short- and long-term studies.

In addition to the major dissolved gases described above, natural and anthropogenic VOCs are also important for studies in coastal regions. Presently, the best method to monitor VOCs is MIMS, which has been successfully used to measure DMS, benzene, toluene, and chloroform in situ (Kibelka et al. 2004, Short et al. 2006). By correlating in situ MIMS data with global

positioning system (GPS) coordinates, researchers were able to identify and quantifiy chemical plumes that may occur when chemicals are released from a point source (Kibelka et al. 2004).

HYDROTHERMAL VENTS

Thriving deep-sea communities are often found surrounding hydrothermal vents. Primary production in these communities is driven by chemosynthesis, the use of chemical energy instead of light for carbon fixation. To understand chemosynthesis and other biogeochemical/geochemical processes at hydrothermal vents, reliable chemical sensors are needed that are capable of measuring sulfide (H_2S/HS^-), O_2, pH, H_2, CH_4, iron and other metals, and additional sulfur species such as FeS, polysulfides (S_x^{2-}), elemental sulfur (S_8), sulfate (SO_4^{2-}), and thiosulfate ($S_2O_3^{2-}$). Because of the dramatic differences in conditions (namely temperature, pressure, and extreme chemical conditions) between vent water and surface waters, the need for in situ chemical analysis is paramount. Sensors employed in hydrothermal vent environments must be able to respond to rapid changes on small spatial and temporal scales, operate under high pressure, and be robust over a range of temperature and chemical conditions as well as resistant to sulfide fouling and corrosion. The ability of a chemical sensor to remain effective over time becomes especially difficult in an environment that is typically rich with microbes and rapidly depositing minerals. Also, any instrument deployed for long-term measurements on the ocean floor would have to consume minimal power because it would be battery powered unless it is connected to a cabled observatory (Daly et al. 2004).

Diffuse Flow Environments

Diffuse flow environments are characterized by temperatures ranging from ambient to ~100°C and a range of chemical conditions. These areas are of interest owing to the abundance of microorganisms and macroorganisms that derive their living via chemosynthesis. Researchers have made significant progress in the development of sensors specifically designed to withstand the harsh conditions found at hydrothermal vents. Chemical species of interest at diffuse flow sites include O_2, H_2S and other reduced S species, H_2, CH_4, and reduced metals. Owing to the highly variable physical nature of these settings, reduced (H_2S) and oxidized (O_2) species often coexist; hence multianalyte sensors are preferred.

Diffuse flow studies using a device on a submersible were conducted among communities around hydrothermal vents using FIA-based colorimetric methods for sulfide, silica, and oxygen (Johnson et al. 1986); sulfide and nitrate/nitrite (Le Bris et al. 2000); and Fe(II) and total Fe (Sarradin et al. 2005). Each analysis was completed on the order of minutes and with spatial resolution on the order of decimeters (Le Bris et al. 2000). These sensor systems appeared quite effective even though precipitation can occur in the FIA tubing if proper precautions are not taken. Additionally, a pH electrode was developed to describe the habitats of vent fauna (Le Bris et al. 2001) because pH dictates the speciation and the subsequent bioavailability of several key chemicals such as (bi)sulfide, pCO_2, and metals to vent organisms.

In situ voltammetric measurements from a system on the *DSV Alvin* have been used at diffuse flow sites by Luther et al. (2001), primarily to describe the chemistry around vent fauna. Solid-state Au/Hg voltammetric microelectrodes (Brendel & Luther 1995) were coupled with a thermocouple to provide quantitative information on a variety of electrochemically active species (**Table 1**) in a single electrochemical scan that is achieved in a matter of seconds (Luther et al. 2008). The instrumentation used in these studies has been modified to operate autonomously, and has been used to monitor O_2 and H_2S for a period of three days (Luther et al. 2008).

Presently, no sensors have proven robust enough for long-term (months to years) data collection in diffuse flow sites, primarily because of power issues. The ability to measure many species with a single sensor on a very short time scale and centimeter spatial scale is invaluable, because the sharp chemical gradients and large fluctuations vent fauna routinely experience may not otherwise be fully realized.

High-Temperature Vents

Hydrothermal vents are important in the global cycling of many chemical species (Edmond et al. 1979) and are a source of reduced materials for chemosynthesizers. For sensors to work in these environments they must withstand large temperature gradients, high pressures, and a wide range in chemical conditions, and be resistant to physical fouling (mineral precipitation).

Ding et al. (2001) have developed selective electrodes robust enough for the in situ measurement of pH, H_2, and H_2S directly in high-temperature hydrothermal vent fluids up to 370°C and 300 bar (**Table 1**). The three electrodes are packaged together with a thermocouple so that all sensing elements are within 0.5 cm of each other for simultaneous measurements (Ding & Seyfried 2007). The electrodes' materials (zirconia ceramic for the pH electrode, Pt or Au for the H_2 electrode, and Ag/Ag_2S for the H_2S electrode) have proven to be robust enough to withstand the extreme conditions of vent fluids. A successful two-day deployment of the H_2 and thermocouple of this sensing package established its stability and showed promise for longer-term deployments (Ding & Seyfried 2007). These are significant developments because pH and H_2 (as a proxy of redox state) are considered master variables essential to understanding the lifetime and evolution of vents. Laboratory studies are ongoing to explore how electrode materials may change over long time periods under the extreme conditions typical of hydrothermal vents (Ding & Seyfried 2007).

Brine separation occurs in hot hydrothermal vents and gives an indication of the state of the vent. Larson et al. (2007) have developed a technique for measuring salinity using conductivity. Because chloride is the main anion in hot vent fluids (sulfate has been consumed during its hydrothermal reduction to sulfide), conductivity is a good proxy for chloride. The cell, which was used for months in a hot vent, was designed with four gold electrodes in a ZrO_2 ceramic housing to overcome the hot temperatures and corrosion to sulfide.

Raman spectroscopy (**Table 1**) has recently been developed as a multianalyte sensor at hydrothermal vents. A system first reported by Pasteris et al. (2004) was designed for the measurement of sulfate, carbonate, and nitrate in hydrothermal vent fluids. DLs are not very low but are adequate for sulfate (1.6 mM) at vents. Complicating the Raman analyses is the possibility of spectral shifts on changes in temperature and pressure; these shifts can be different for each dive (Brewer et al. 2004). However, a diamond standard placed in the laser path of the deep ocean Raman in situ spectrometer (DORISS) (Brewer et al. 2004) allows for shift correction. DORISS has been effectively applied to study sulfate and mineral deposits (White et al. 2005). The power demands of current Raman systems are too high for them to be effectively used without a large power source or tether. However, the miniaturization of a commercially available Raman system has also been tested in simulated hydrothermal vent fluids (Dable et al. 2006) and shows promise.

CONCLUSIONS

In this short review, we have attempted to indicate the methods presently available and necessary for the measurement in marine waters of dissolved chemical species that are essential for biochemical processes. For the upper ocean and interface regions (oxic/suboxic and suboxic/anoxic), there is a need to extend DLs for nutrients and micronutrients to (sub)nanomolar levels and increase

selectivity to natural chemical interferences. For pH and chemical species in higher concentrations such as dissolved gases, better precision is required to adequately address biochemical processes. There is a need to measure many chemical species simultaneously in the same water mass, and more work is needed in this area for a variety of techniques (e.g., IR, Raman, mass spectroscopy, voltammetry, laser induced breakdown spectroscopy, gas and liquid chromatography). Multielement methods are particularly good for observing how two or more analytes vary with time. In dynamic systems such as hydrothermal vents (and rapidly changing interfaces), the response time of the sensor must be fast (seconds in some instances) to detect analyte variation with time. Power consumption is a major concern for instruments deployed on moorings and mobile assets, so much work is needed to miniaturize instrument components to reduce power needs. Sensors must be robust to withstand extremes in temperatures, pressure, and corrosive chemicals (e.g., H_2S) while operating for longer time intervals.

Clearly there is much work that needs to be done in many areas of sensor development and for a variety of marine environments. Also, we have not discussed data reduction and management needs for sensor deployments on observatories.

DISCLOSURE STATEMENT

The authors are not aware of any biases that might be perceived as affecting the objectivity of this review.

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Errata

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