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Instruments and Methods

Development of a deep-sea laser-induced breakdown spectrometer for in situ multi-element chemical analysis

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ABSTRACT

Spectroscopy is emerging as a technique that can expand the envelope of modern oceanographic sensors. The selectivity of spectroscopic techniques enables a single instrument to measure multiple components of the marine environment and can form the basis for versatile tools to perform in situ geochemical analysis. We have developed a deep-sea laser-induced breakdown spectrometer (Chemi-Cam) and successfully deployed the instrument from a remotely operated vehicle (ROV) to perform in situ multi-element analysis of both seawater and mineral deposits at depths of over 1000 m. The instrument consists of a long-nanosecond duration pulse-laser, a spectrometer and a high-speed camera. Power supply, instrument control and signal telemetry are provided through a ROV tether. The instrument has two modes of operation. In the first mode, the laser is focused directly into seawater and spectroscopic measurements of seawater composition are performed. In the second mode, a fiber-optic cable assembly is used to make spectroscopic measurements of mineral deposits. In this mode the laser is fired through a 4 m long fiber-optic cable and is focused onto the target's surface using an optical head and a linear stage that can be held by a ROV manipulator. In this paper, we describe the instrument and the methods developed to process its measurements. Exemplary measurements of both seawater and mineral deposits made during deployments of the device at an active hydrothermal vent field in the Okinawa trough are presented. Through integration with platforms such as underwater vehicles, drilling systems and subsea observatories, it is hoped that this technology can contribute to more efficient scientific surveys of the deep-sea environment.

1. Introduction

The application of manned submersibles and remotely operated vehicles (ROVs) to sampling has led to great advances in our understanding of deep-sea geochemical processes, since they allow for accurately geo-referenced chemical information to be obtained from samples whose origins and context are known. However, the number of samples that can be retrieved limits the range and spatial resolution of the information obtained, and the information is not immediately available for feedback since the analysis is typically performed in a laboratory. Recent advances in measurement technology and vehicle infrastructure have seen the successful application of in situ sensors whose measurements can increase the spatial and temporal resolution of chemical information, and enable informed decisions to be made based on real-time data (Okamura et al., 2001; Fukuba et al., 2009; Luther et al., 2001; Nuzzio et al., 2002; Provin et al., 2013). Most of these techniques, however, are limited to measurement of a single target element or molecule that is dissolved in seawater. On the other hand, spectroscopy is rapidly emerging as a versatile tool that can expand the envelope of modern oceanographic sensors. Spectroscopy allows for non-contact multivariate analysis, with a large variety of interactions that can be applied to probe different aspects of the deep-sea environment. Laser Raman (LR), a technique based on non-linear scattering of light, has been used to study the molecular chemistry of gases dissolved in seawater and also measure the composition of gas hydrate complexes at depths of up to 3600 m using a deep-sea LR probe developed by the Monterey Bay Aquarium Research Institute (MBARI) (Brewer et al., 2004; Zhang et al., 2010). In this paper, we describe the development of a 3000 m depth rated Laser-induced breakdown spectrometer and its deployment from a ROV at a deep-sea hydrothermal vent field in the Okinawa trough. The

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instrument is capable of measuring the elemental chemical composition of both fluids and solid deposits, and so can be used to study different aspects of deep-sea geochemistry compared to the LR technique, which is effective for looking at molecular chemistry. The requirements to obtain high quality signals underwater and at oceanic pressures using laser-induced breakdown spectroscopy (LIBS) are described and we discuss the engineering developments that were necessary to make the instrument field operational. The results of controlled laboratory experiments are presented together with data processing techniques that have been developed to interpret the signals in a scientifically useful way. Spectra obtained during deployments at sea demonstrate the unique ability of the instrument to perform in situ, multi-element chemical analysis of seawater and mineral deposits at depths of over 1000 m. Finally we discuss directions for future developments regarding instrumentation and signal processing methods and describe potential application areas for the device.

2. Underwater LIBS at high pressure

LIBS is a form of atomic emission spectroscopy (AES) that focuses a high power laser-pulse to generate a plume of excited material. The excited material, or plasma, emits specific wavelengths of light that correspond to the atoms and ions that compose the plume. The method can, in principle, detect all elements if sufficiently high excitation temperatures can be achieved (Miziolek et al., 2006). An advantage of this method is that it allows for real-time analysis of gases, liquids and solids with no requirement for sample preparation, making it an attractive technique for in situ analysis. LIBS can probe different aspects of the deep-sea chemical environment compared to the LR technique, since it measures elemental, not molecular, composition. The two methods are essentially complementary, however, while not all materials are Raman active, LIBS can in theory measure the composition of any target since all matter is composed of elements. The advantages of LIBS for in situ analysis has been recognized by several groups and it has found application in the field for environmental soil monitoring (Wainner et al., 2001; Harmon et al., 2005; Yamamoto et al., 1996; Mosier-Boss et al., 2002), survey of nuclear power plants (Whitehouse et al., 2001; Saeki et al., 2014) and recently planetary exploration (Wiens et al., 2002, 2012; Maurice et al., 2012; Meslin et al., 2013).

Studies of underwater LIBS however, often report strong confinement and plasma quenching effects due to the nearly incompressible fluid medium, which can significantly degrade the quality of the signals obtained. The interactions within the optically dense plasmas generated underwater are far from ideal for spectroscopy (Sakka et al., 2002; Pichahchy et al., 1997). In order to overcome this problem, most studies concerning underwater LIBS have used a double-pulse technique (Nyga and Neu, 1993; De Giacomo et al., 2005; Lazic et al., 2005, 2007), where a first pulse is used to create a cavity into which a second pulse is delivered, allowing mechanisms similar to LIBS in a gas to take place. However, several studies have reported that this method is sensitive to external pressure, with pressures of just a few MPa, corresponding to depths of a few hundreds of meters, having a significant detrimental effect on the analytical value of the signals obtained (Lawrence-Snyder et al., 2007; Michel and Chave, 2008b; De Giacomo et al., 2011; Takahashi et al., 2013). This had ruled out the possibility of applying LIBS to in situ chemical analysis in high-pressure liquid environments such as the deep-sea. However, studies at the Woods Hole Oceanographic Institution demonstrated for the first time, that with an appropriate setup, narrow spectral lines can be observed from plasmas generated directly in bulk ionic solutions at high pressures of up to 30 MPa using a conventional single-pulse (Michel et al., 2007; Michel and Chave, 2008a). Similar results have also been reported independently by our group (Masamura et al., 2011) and the Ocean University of China (Hou et al., 2014). In Thornton and Ura (2011), the authors further demonstrated that narrow spectra can be observed from water immersed solids using a single-pulse with no significant effect of pressure up to 30 MPa. The difference in behavior observed for the single and double-pulse methods at high hydrostatic pressures has been linked to the transient pressure shockwaves generated when a high power laser-pulse is focused in a nearly incompressible medium such as water (Thornton et al., 2012a, 2013, 2014a). Based on these findings, we developed a prototype In situ Seafloor Element Analyzer (I-SEA), which is capable of both single and double-pulse LIBS measurements. The system was deployed in the Kagoshima bay at a depth of 200 m during March 2012 (Thornton et al., 2012b). During the experiment, the instrument was deployed from an ROV and measurements were performed using a single pulse. Successful measurements of seawater composition were achieved. While emission spectra were also observed from solid test pieces mounted on the ROV, the quality of the signals obtained was poor compared to controlled laboratory experiments performed using the same specimens underwater at the same hydrostatic pressure. The difference in quality was attributed to difficulty in focusing the instrument on a solid surface using a ROV manipulator, combined with the sensitivity of underwater measurements using a conventional single-pulse to surface roughness.

The next major development took place when it was demonstrated that the long-pulse laser excitation technique, which uses a single-pulse of duration ~150 ns (Sakka et al., 2006, 2009, 2014), can offer significant enhancements in signal quality compared to a conventional single-pulse (with pulse durations of <20 ns) for both solids immersed in water (Thornton et al., 2013) and also bulk ionic solutions (Thornton et al., 2014a). In both cases, no significant degradation in signal quality was seen for external pressures up to 30 MPa. While the authors are presently investigating techniques to further optimize LIBS measurements in high pressure underwater environments, our present setup using the long-pulse technique has detection limits in the order of tens of μmol/kg for certain species in dissolved ionic solutions and in the range of 0.1–1.0 wt% for certain elements in seawater immersed solids. These limits are sufficient for detection of several major elements in seawater and hydrothermal fluids (Kennish, 2000; Kawagucci et al., 2011) and mineral deposits (Ueno et al., 2003) found in volcanically active areas of the seafloor. Based on these studies, we have developed our 2nd generation LIBS device, called the ChemiCam (Chemical Camera), that incorporates a long-pulse laser and addresses several of the issues identified through operation of I-SEA. It should be noted that while the name of the device is similar to the Los Alamos National Laboratory's ChemCam (Maurice et al., 2012), deployed on the Mars Science Laboratory (MSL) rover Curiosity, the devices are unrelated and their developments have been independent of each other. The jump from laboratory demonstration to field deployment of ChemiCam has not been trivial. While the prototype I-SEA was built using commercially available lasers and spectrometers, the components of ChemiCam are almost entirely custom made. In particular, the specifications of the long-pulse laser used in the laboratory experiments (Sakka et al., 2006, 2009, 2014; Thornton et al., 2013, 2014a) are not met by any commercially available laser and a significant investment of effort was required to develop a robust, compact long-pulse laser that can be incorporated into a field deployable LIBS instrument. While the application of a long-pulse laser is seen as the key technology for the realization of deep-sea LIBS, a number of other technical issues have also been overcome and are described in the next section.