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Application of laser-induced breakdown spectroscopy to Arctic sediments in the Chukchi Sea

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ABSTRACT

Physical and geochemical investigations coupled with laser-induced breakdown spectroscopy (LIBS) were performed on three surface sediment cores (ARA02B/01A, ARA02B/02, and ARA02B/03A) recovered from the western Arctic Ocean (Chukchi Sea) during the IBRV ARAON 2011 expedition. The LIBS technique was applied to conduct elemental analysis of the Arctic sediments and compare the results to those obtained using an X-ray fluorescence (XRF) core scanner and inductively coupled plasma (ICP) system. The LIBS technique showed an elemental composition similar to that using XRF and ICP in each sediment core. Qualitative and semi-quantitative LIBS analyses provide distinguishable patterns between sediment cores, similar to those observed in the ICP analysis. In particular, the elemental pattern of LIBS responded to the color change of the sediment cores. Dark brown layers in the upper parts of the cores were indicated by the color indices and showed elevated Mn/Al ratios, suggesting the influence of regional variation in terrestrial input since the deglacial period. In this study, grain size distribution and contents of detrital dolomite and organic carbon as well as elemental composition (LIBS) were considered to determine sediment provenance and sedimentation environments during the Holocene. Furthermore, the present study showed that the LIBS technique may be used as an applicable method to unravel regional variations in sedimentary composition in the Arctic Ocean.

1. Introduction

Many common approaches (e.g., electron probe X-ray microanalysis, inductively coupled plasma, laser induced breakdown spectroscopy, scanning electron microscopy-energy dispersive spectrometry, X-ray fluorescence, etc.) are used to determine the presence of elements in materials. Particularly, current laser induced breakdown spectroscopy (LIBS) systems promote simplicity with on-site measurement [1] unlike other techniques that require time-consuming and complicated sample preparation steps as well as expensive equipment and trained operators. Indeed, the LIBS technique that analyzes the spectral emission of a chemical element from laser-induced plasma has been applied to geological survey on Mars. There is growing interest in the technique, largely because of its simple or absent sample preparation as well as a rapid, less-destructive, and cost-effective screening method for various natural materials ([2] and references cited therein). Similar to other common methodologies, quantitative measurement using LIBS requires standard reference materials, but the certified reference materials are difficult to apply to geological samples (rocks, soils, and sediments) [3]. Although standard-free LIBS approaches using a calibration model or matrix-similar standards has been suggested, it needs considerable developmental effort to be applied to diverse and heterogeneous materials [3]. In application to geological materials, the accuracy of the LIBS technique is influenced by the matrix effect (water content and grain size), but the matrix effect can be minimized by sieving and pelletizing materials [4].

Geochemical investigation based on elemental compositions of marine sediments has been conducted to track climate change at a geological timescale. Indeed, Antarctic marine sediments, analyzed using LIBS, have implied that the LIBS technique may be used to identify sediment provenance in the polar seas [5]. LIBS may be an ideally applicable method for geologists to estimate elemental distribution in marine

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sediments, but its applications are limited. Moreover, there is no feasibility study for Arctic marine sediments using the LIBS technique to compare it to traditional approaches such as X-ray fluorescence (XRF) core scanning and inductively coupled plasma (ICP) measurement.

The Arctic Ocean has recently become an important issue due to a rapid reduction in sea-ice extent that globally affects ocean circulation and climate change [6,7]. In particular, the North Pacific inflow from the shallow and narrow Bering Strait (hereafter Bering Strait inflow; BSI) plays an important role in controlling heat, freshwater, and nutrient fluxes to the western Arctic Ocean, and it was highly susceptible to sea-level fluctuations during the late Quaternary ([8,9] and references cited therein). Thus, the BSI signal can provide a means to understand variations in sea-ice and marine production in the western Arctic Ocean [9]. The Bering Strait may have been predominantly closed by the end of the last glacial period (80 000–11 000 years before present) [10]. The lowered sea-level during the last glacial period may have resulted in the limited influx of fresher Pacific Ocean waters into the Arctic Ocean. Although the history of sea level in the Bering Strait has been previously described [11–13], the inflow of Pacific waters during the post glacial period (Holocene) has been poorly estimated because of the lack of high-resolution records. Sediment properties have been used to reconstruct paleoclimatic events in the Arctic Ocean ([14,15] and references cited therein). For example, sediment color is generally sensitive to bottom water conditions (such as water depth, Eh, and pH), sediment constituents (such as disseminated organic matter, microbe, and carbonate), and/or diagenesis, texture, and composition of minerals and elements in sediments. In general, mineral and elemental compositions are related to sediment grain size and provenance. Recently, Kobayashi et al. [15] investigated the mineral distribution and color indices of Arctic sediments, and reported that mineral composition is useful for tracking sediment provenance associated with the BSI signal. Moreover, the elemental distribution of Arctic sediments is presumably related to riverine discharge from the hinterland, ice rafted debris (IRD), and ocean circulation in the western Arctic Ocean [14]. In particular, Meinhardt et al. [14] reported that dark brown layers in Arctic surface sediments show an excessive amount of Mn and Fe, and a distinct change in Mn/Al and Fe/Al ratios seems to reflect a climatically elevated input of Mn and Fe near the sediment/water interface during the late Quaternary interstadial or interglacial periods.

The aim of the present study is to evaluate the feasibility of using the LIBS technique to analyze Arctic sediments. Three surface sediment cores were recovered from the western Arctic Ocean (Chukchi Sea) during the IBRV ARAON 2011 expedition. Physical and geochemical datasets, such as elemental composition (LIBS), grain size distribution, color indices, and organic carbon content, were analyzed for the sediment cores. In particular, the elemental profiles of LIBS were compared to those measured using an ITRAX XRF core scanner and ICP.

2. Materials and methods

2.1. Field description and sample preparation

Three coring sites from the shelf toward the Chukchi Plateau (ARA02B/01A, ARA02B/02, and ARA03B/03A in Fig. 1a) were selected to obtain sediment cores using a multiple- and box-corer during the IBRV ARAON 2011 expedition (ARA02B). Three box cores were sealed on board for further XRF-core scanning (ITRAX). Every three parallel cores were retrieved from the same multiple-corer at each coring site. A set of the parallel cores was assigned to the present study (here referred to as 01A, 02, and 03A), and the others were kept at the Korea Polar Research Institute (KOPRI) or transferred to Hokkaido University [15]. Cores 01A, 02, and 03A were subsampled at a depth interval of 2 cm and stored in a freezer onboard until undergoing a freeze-drying process. The freeze-dried sediments from the three multiple cores were all used for LIBS, ICP, and grain size analyses, and sediments of the 03A core were additionally analyzed using the Delta V elemental analysis - isotope ratio mass spectrometry (EA-IRMS) at KOPRI.

2.2. Sediment analysis

Box cores were split in the laboratory and the split core surfaces were run through an ITRAX core scanner at KOPRI to obtain XRF

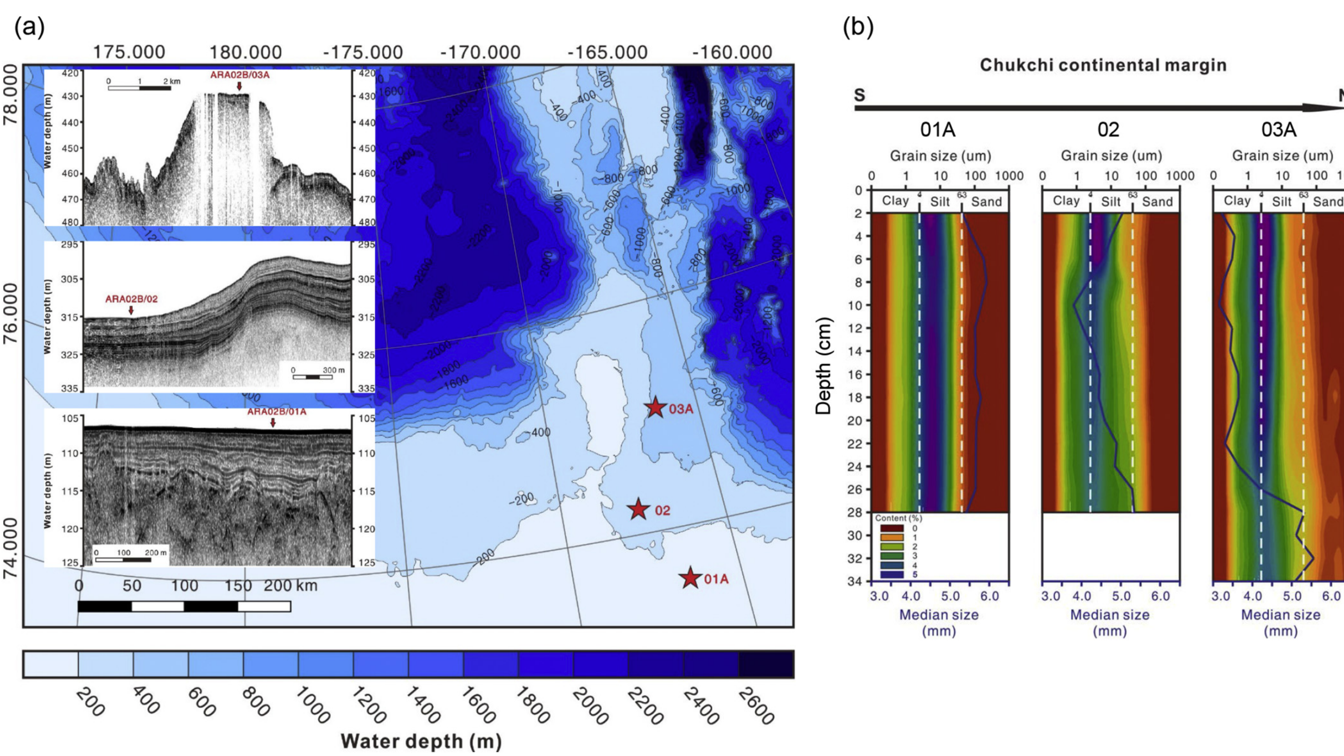

Fig. 1. Description of coring locations with (a) SBP image, and (b) grain size for sediment cores.