論文題目　Quantitative elemental analysis of water-submerged solids:
Temperature segmented multivariate regression of laser-induced plasma emissions
（レーザー誘起プラズマ発光を用いた温度セグメント化回帰モデルによる
水中固体中元素定量分析手法）

氏　　　名　　　髙橋　朋子

Introduction

In this study, quantitative elemental analysis of water-submerged solids is investigated for applications to in-situ measurements of deep-sea rocks. Deep-sea mineral resources, in particular hydrothermal vents, are the focus of much attention due to their unique geological characteristics as well as their potential for future industries. While sampling of deep-sea sediments and rocks is required for detailed knowledge of the distribution, it takes significant time and cost due to the inaccessibility of the deep-sea. While in-situ techniques for measurements and monitoring of dissolved ions and compounds of seawater have been developed [1], in-situ measurements of solids remain limited.

LIBS applications to deep-sea environments

Laser-Induced Breakdown Spectroscopy (LIBS) has potential for in-situ measurements of deep-sea rocks, since targets can be rapidly analyzed without sample preparation. LIBS is a form of atomic emission spectroscopy that analyzes light emitted from atoms and ions of ablated materials in a plasma created by high intensity pulse laser, and has been applied to in-situ analysis on land and for planetary explorations [2]. Signal degradation at a water-submerged samples measured using a conventional laser pulse or a double pulse technique at high water pressures, can be improved using a long laser pulse with duration of $\geq$ 100 ns [3]. Using the long-pulse LIBS technique, in-situ identification of major elements of hydrothermal deposits at depths more than 1000 m has been successfully performed [3]. However, quantification of elements using LIBS is still a challenging task. Multivariate analysis, in particular, partial least squares regression analysis (PLS), which can statistically extract information related to concentrations from the signals as latent variables (LV), has been applied to in-situ LIBS applications [4]. When PLS is applied directly to underwater LIBS signals, the accuracy was found to be unsatisfactory, due to large shot-to-shot fluctuations of signals [5]. In this study, in order to improve the performance of quantitative analysis for water-submerged solids, segmentation of database by excitation temperature (hereafter temperature) is proposed.

Proposed method

Temperature differences have a significant influence on the signals compared to the electron number density as seen in Fig. 1 (a) and (b). It was also found that the range of temperatures is spread more widely in water than in air. In the proposed method, the effect of temperature is taken into consideration by dividing a database into segments which contain only spectra within a defined temperature range. A separate PLS model is constructed for each segment and the compositions of an unknown sample are calculated using a model of the appropriate segment, which is determined by calculating temperature from the spectrum of the unknown sample. In addition to the proposed method, the effects of different signal processing methods (normalization, smoothing, background subtraction, and the combination of these steps) on reducing errors in PLS calculations are investigated. The accuracy of the models was determined by root mean square errors of cross validation (RMSECV), and regression lines.

Experimental setup

The experimental setup is shown in Fig. 2. The plasma was generated by a Q-switched Nd:YAG long-pulse laser with wavelength of 1064 nm delivered via a fused-silica fiber. The targets were submerged in pure water for metal and in seawater for rock samples. Spectroscopic measurements were performed using a spectrograph and an intensified charged-coupled device (ICCD). Cu and Zn in brass samples and powder samples of sulfide rocks taken at hydrothermal vents were quantified.

Results of PLS regression models

RMSECV and slopes are shown in Fig. 3 (a) and (b) for metals, and (c) and (d) for rocks, respectively. The black and red bars indicate values of Cu and Zn. Labels "raw", "norm", "smooth", "bg", "all", "7000", "7500", "8000", and "8500" indicate raw spectra, spectra with normalization, smoothing, background subtraction, all steps, the temperature segmentation from 6750 to 7250 K, from 7250 to 7750 K, 7750 to 8250 K, and 8250 to 8750 K, respectively. Spectra
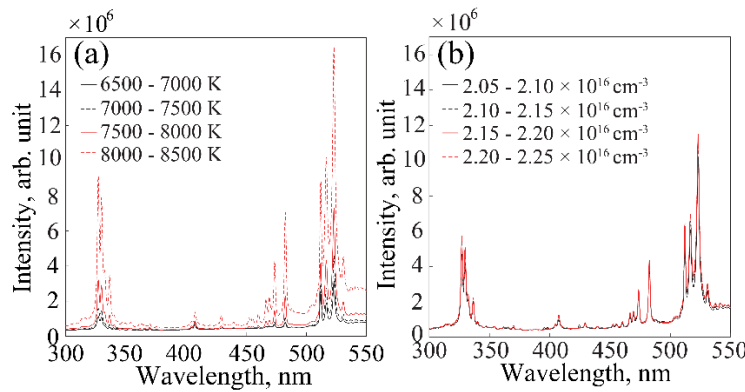

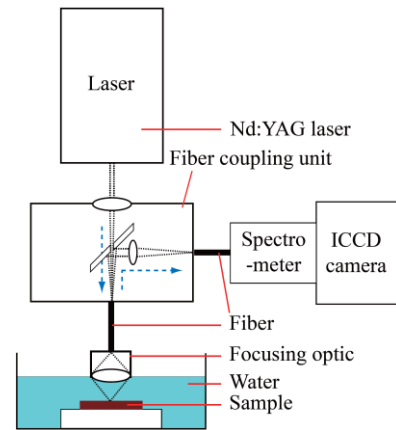Fig. 1 Spectra for (a) different temperatures and (b) different electron number densities.

Fig. 2 Experimental setup.

with all signal processing steps were used for temperature segmented models. 11 brass samples and 18 rocks were used for the analysis. From the results, it was found that normalization is most effective among signal processing methods investigated in this thesis to improve the accuracy with ~ 60 % RMSECV reduction compared to non-segmented model. It was found from the analysis of LVs that background fluctuations are mitigated by normalization, and so peaks were successfully extracted in LVs. Rocks showed the similar trend, while the effect of normalization was not as strongly seen as metals. It was found that the effect is limited to the complex spectra which have large peak and background fluctuations due to a number of peaks from other elements than modelled. As for the temperature segmentation, appropriate segment ranges, which were the highest for metals and intermediate range for rocks, showed further improvement of the accuracy, with 43 % and 25 % RMSECV reduction for Cu and Zn in metals and 26 % and 32 % for Cu and Zn in rocks, respectively. The highest temperature range for rocks had worse accuracy due to peak broadening which is caused by high electron number density. From the results, it can be said that the temperature range should be high enough for sharp peak detection and multi-peak excitation, but at the same time it should be low enough to obtain spectra without significant peak broadening. In addition, it was found from the study of rocks, that the database should be constructed by a large number of samples, which have the similar matrix to a sample. This finding is in agreement of the study of Martian rocks in low-atmosphere environments [4], and appears to be a consistent trend for field application of quantitative LIBS.

While the proposed method was found to be effective to rock samples, fluctuations of predicted concentrations among different sets were larger than metals. It might be partly because of shot-to-shot fluctuations caused by inhomogeneous properties of rock samples. Since the
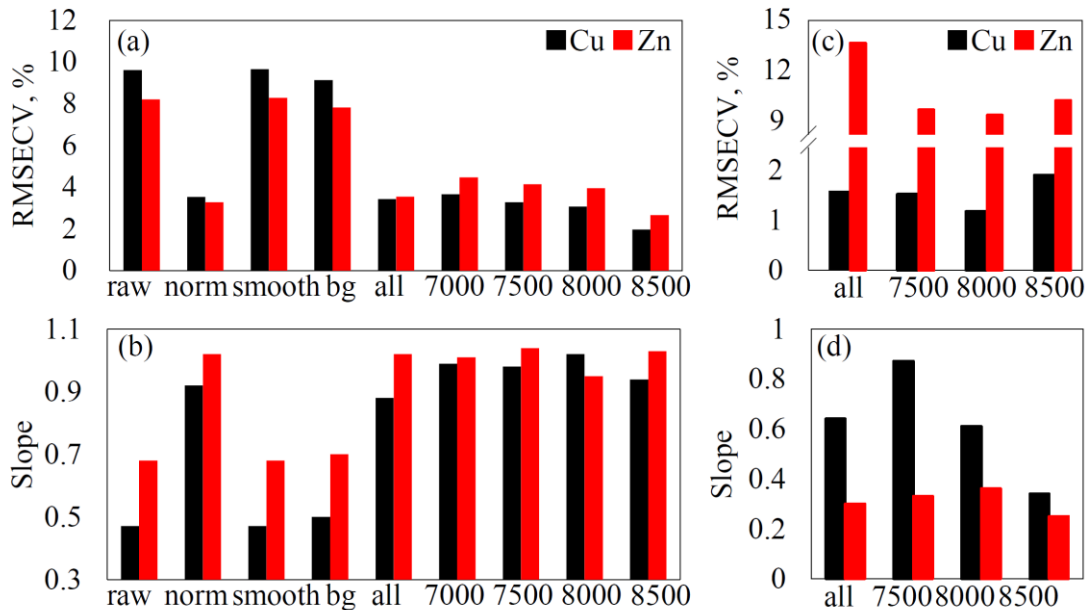

Fig.3 PLS results of signal processing steps and temperature segmentation. (a) and (c) show RMSECV of metals and rocks, and (b) and (d) show slopes of metals and rocks.

ablation mass is significantly small, which is ng order, compared to mg order for methods for actual concentrations. The variation of surface chemical compositions should be more accurately evaluated by using a chemical mapping technique with high spatial resolution, such as X-ray fluorescence (XRF) analysis. While further investigations are required, it is still realistic to apply this method to deep-sea applications considering the range of obtained accuracy.

Conclusions and future studies

In this thesis, database segmentation by temperature was proposed for the method which can reduce effects of shot-to-shot fluctuations of underwater LIBS signals on PLS. It was found that sharp peak extraction in LVs are important for obtaining accurate PLS models. In this study, peak and background fluctuations were mitigated by normalization, and for further improvement, the proposed database segmentation with the appropriate temperature range, in which peaks are sharply detected, was effective. Also, it can be said that the database should be constructed by the large number of samples with the similar matrix of a sample.

For further evaluation of the accuracy, the inhomogeneity of samples should be taken into account by using a surface mapping technique. While it can be considered that the appropriate temperature segmentation is also applicable to other elements since it focuses on peak separation and extraction in LVs, not only temperature but also other factors, such as the degree of peak broadening, should be included in the criteria for segmentation.

The whole process from data acquisition and optimization of experimental and analytical conditions, to quantitative interpretation of signals can be automated using the investigated method in this study. This indicates that LIBS chemical analysis of seafloor deposits can potentially be completely automated through the use of AUVs, which will be a game-changing technique for deep-sea surveys.

The study contributes to development of a technique for the applications of deep-sea LIBS, and to scientific understanding of underwater laser-induced plasmas.

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