Laser ablation inductively coupled plasma mass spectrometry for quantitative imaging of elements in ferromanganese nodule

Junichi Hirata [a], Kazuya Takahashi [b], Yu Vin Sahoo [b], Miho Tanaka [a,*]

[a] Graduate School of Marine Science and Technology, Tokyo University of Marine Science and Technology, 4-5-7 Konan, Minato-ku, Tokyo 108-8477, Japan
[b] RIKEN, 2-1 Hirosawa, Wako, Saitama 351-0198, Japan

ABSTRACT

Laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) is used for the quantitative elemental imaging of ferromanganese nodules to obtain the distributions of both major and trace elements, owing to its high sensitivity and wide dynamic range. Methods for obtaining a calibration line, using Mg as an internal standard for correction, and data treatment were developed for the quantitative imaging of elements in ferromanganese nodules. The validity of the values determined by LA-ICP-MS was confirmed by comparison with elemental contents obtained by ICP-MS. A two-dimensional plotting system for LA-ICP-MS was established for expressing elemental contents as colors along with spatial information. The simple method describes the ease with which the colors can be changed to define the content ranges of elements, and the elemental distributions show the layered structure, clearly depicting the contrast. Reproducibility of these analytical processes was also confirmed by analyzing two ferromanganese nodules. The method is expected to be a powerful tool for investigating paleo-environmental changes in the region surrounding a ferromanganese nodule and its formation processes.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

Advances in techniques for analyzing elemental contents at trace levels are a boon in current research. Generally, these techniques examine the total metal content after the homogenization and digestion of samples but do not provide sufficient information on the spatial distribution of elements. Laser ablation inductively coupled plasma mass spectroscopy (LA-ICP-MS) is a popular technique of elemental imaging for solid samples (Barst et al., 2011; Becker et al., 2014; Konz et al., 2012, 2013; Lear et al., 2012; Moreno-Gordaliza et al., 2011; Urgast et al., 2012; Wang et al., 2013; Zhu et al., 2012). In contrast to destructive methods of analysis, LA-ICP-MS enables the spatial resolution of a small amount of a sample. The LA system provides a micro sampling method for solid samples as an alternative to the conventional "micro spatula" or a "micro drill", whereby information at the micro sampling point can be obtained and the structure near the sampling point is preserved. Through observation by a CCD camera and micro sampling with a laser, the contents of elements in the sample can be obtained along with their spatial distribution. Therefore, elemental imaging by LA-ICP-MS provides important information on solid samples. In addition, the direct sample introduction system used in LA-ICP-MS prevents samples from contamination with reagents required for sample dissolution (Fernández et al., 2010; Shaheen et al., 2012). Other methods, such as

electron probe micro analyzer (EPMA), scanning electron microscope-energy dispersive X-ray spectroscopy (SEM–EDX), and secondary ion mass spectrometry (SIMS), can be used with solid samples, but a high-vacuum system is required, whereas the LA-ICP-MS analysis can be performed at atmospheric pressure. A high vacuum destroys the structure of samples with a high moisture content, such as oceanic sediment by dehydration. Thus, LA-ICP-MS enables the spatial resolution analysis using only a small amount sample introduction system, and LA-ICP-MS prevents samples from contamination and dehydration.

Ferromanganese nodules are found on the seafloor. They have characteristic layered structures and scavenge trace elements in sea water, such as rare-earth elements (Duliu et al., 2009; Hein et al., 2013). These nodules are extremely good indicators of environmental changes, especially the elemental contents and distributions in their complicated layered structure. Previous studies on ferromanganese samples (ferromanganese nodules and crusts) include the bulk analysis of major and trace elements by instrumental neutron activation analysis (INAA), ICP-atomic emission spectrometry (ICP-AES), and ICP-MS (Aplin, 1984; Carlo and McMurtry, 1992; Glasby et al., 1987; Kunzendorf et al., 1993), the analysis of ferromanganese samples by a sequential leaching method to investigate how trace elements are scavenged by Mn and Fe oxides or hydroxides (Koschinsky and Halbach, 1995; Koschinsky and Hein, 2003; Mohwinkel et al., 2014), analysis of the distribution of major elements by EPMA, SEM–EDX, and micro area X-ray diffractometer (μXRD) (Gasparatos et al., 2005; Manceau et al., 2003; Palumbo et al., 2001; Wang et al., 2012), analysis of the chemical structure of Mo by X-ray absorption fine structure (XAFS) (Kashiwabara

* Corresponding author at: Tokyo University of Marine Science and Technology, 4-5-7 Konan, Minato-ku, Tokyo 108-8477, Japan.
E-mail address: mihotnk@kaiyodai.ac.jp (M. Tanaka).

et al., 2009), and the determination of the age of a ferromanganese nodule by a dating method using $^{10}Be/^{9}Be$ (Frank et al., 1999; von Blanckenburg et al., 1996). In previous studies, various types of information have been accumulated on ferromanganese samples, such as classification of their origins, chemical compositions, and growth rate. However, the formation processes of ferromanganese nodules and paleo-environmental changes are yet to be studied. To elucidate this, not only averaged elemental content but also elemental distribution is required. Distribution of elemental contents is considered as significant basic information on ferromanganese nodules. For example, geochemical parameters can be calculated from elemental contents by preserving chronological order in the layered structure and the data obtained allows the analyst to decide exact position to be examined for isotope ratio analysis (Bollhöfer et al., 1996). Thus, although elemental distributions in the layered structure have been studied (Gasparatos et al., 2005; Manceau et al., 2003; Palumbo et al., 2001; Wang et al., 2012), the distribution of trace elements in the layered structure has not been investigated owing to analytical problems.

Information on the scavenging mechanism of elements by ferromanganese nodules could throw light on the process, which could be artificially produced, thus applying ferromanganese nodules as scavengers of metals in waste water. To achieve this, first both the major and trace elements at a small point on the surface were analyzed by applying a laser shot. A spatial resolution analysis is very important at the borders of the layered structures to elucidate changes in the environment, which give the time of formation of each layer. Second, to investigate the environmental changes and formation processes of ferromanganese nodules, sample structures are preserved in the analytical procedures. In previous studies, the elemental imaging of major elements in ferromanganese samples by EPMA, SEM–EDX, and μXRD was reported (Gasparatos et al., 2005; Manceau et al., 2003; Palumbo et al., 2001; Wang et al., 2012) but, owing to the low sensitivity of these methods, it was difficult to analyze trace elements such as rare-earth elements. ICP-MS, which can analyze both major and trace elements owing to its high sensitivity and wide dynamic range, was applied for spatial resolution analysis in small spaces of a ferromanganese nodule. From the above considerations, LA-ICP-MS is the most suitable method for the elemental imaging of ferromanganese nodules, as a sample is ablated at atmospheric pressure then directly introduced into the MS detector.

In previous studies on elemental imaging using LA-ICP-MS, the elemental imaging data were expressed as semiquantitative values, such as peak intensities and peak intensity ratios (Barst et al., 2011; Konz et al., 2013; Moreno-Gordaliza et al., 2011; Urgast et al., 2012; Wang et al., 2013; Zhu et al., 2012). To perform detailed data analysis, imaging data was expressed quantitatively. Quantitative elemental imaging by LA-ICP-MS has been reported, however, the studies have been limited to the field of biological samples (Becker et al., 2014; Konz et al., 2012; Lear et al., 2012). It is difficult to determine and image elements in geological samples like ferromanganese samples, because matrices in geological samples are complicated for each sample. In previous studies on a ferromanganese nodule, a powdered bulk sample was investigated, or spatial resolution analysis was performed in a straight line (in one dimension) across the layers by LA-ICP-MS (Axelsson et al., 2002; Garbe-Schönberg and McMurtry, 1994; Hlawatsch et al., 2002; Hirata et al., 2013; Hirata and Tanaka, 2014; Hoffmann et al., 1997; Zhi et al., 2007). The quantitative two-dimensional imaging of elements in a ferromanganese nodule by LA-ICP-MS has not been accomplished owing to technical problems.

Using the LA system for micro sampling, not only ferromanganese nodules but also other geological samples can be imaged. However, measurements using an LA-ICP-MS system involve various problems yet to be solved. A sample is ablated by a laser, the generated nanoparticles are transported to the ICP torch by Ar or He gas, and elemental fractionation occurs through these processes (Koch and Günther, 2011; Russo et al., 2002; Shaheen et al., 2008). Therefore, to determine the elemental compositions in samples, matrix-matched standards

were prepared. In addition to the problem of elemental fractionation, the rate of introduced sample to ICP torch is unstable due to hardness of sample, defocusing of laser, and sampling position in the sample cell (Fricker et al., 2011; Koch and Günther, 2011; Russo et al., 2002; Shaheen et al., 2008). To obtain accurate elemental distributions and elemental contents, discrepancies in the sample introduction rate were corrected.

The aim of this study is to establish a quantitative elemental imaging method of analysis using LA-ICP-MS. For this purpose, the preparation of standards, the correction of unstable sample introduction, validation of the reliability of determined values, and expression of the elemental content in two-dimensional imaging data were performed. Furthermore, these procedures were applied for two different ferromanganese nodules, to confirm the reproducibility of the analytical method. Thus, LA-ICP-MS for quantitative imaging of elements in ferromanganese nodules was established.

2. Experimental

2.1. Reagents

JMn1 (Dulski, 2001; Terashima et al., 1995) was employed as a geological reference material for ferromanganese nodule and was provided by Geological Survey of Japan (GSJ). JMn1 and high-purity manganese dioxide (MnO_2) powder (99.5%, Wako Chemical Co.) were used in the preparation of standards for LA-ICP-MS analysis.

To dissolve a powdered ferromanganese nodule, HNO_3, HCl, and HF (Kanto Chemical Co., ultra pure grade) were used. XSTC-1, XSTC-8, and XSTC-469 (SPEX Certi. Prep.) standard solutions were used for determining the elemental contents in the dissolved sample by ICP-MS. For the determination of Mg and Co, analytical-grade standard solutions (Kanto Chemical Co.) were used. The indium and bismuth solutions used for internal standard were analytical-grade (SPEX Certi. Prep. or Kanto Chemical Co.).

2.2. Instrumentation

High-resolution ICP-MS (ELEMENT XR, Thermo Fisher Sci. Co.) was used to analyze the dissolved ferromanganese nodule. For elemental imaging analysis, a laser ablation system (UP213, New Wave Research Co.) equipped with an ICP-MS system was used. The operating parameters for LA-ICP-MS are shown in Table 1.

Table 1
Operating parameters for LA-ICP-MS.

Parameters	
UP213 (New Wave Research Co.)	
Laser	Nd; YAG
Wavelength	213 nm
Spot diameter	100 μm
Repetition rate	20 Hz
Fluence	1.54–1.73[a] or 4.01–4.43[b] J/cm²
Laser energy	0.121–0.137[a] or 0.314–0.348[b] mJ
Scan speed	100[a] or 50[b] μm/s
Carrier gas flow rate (Ar gas)	1.23 L/min
ELEMENT XR (Thermo Fisher Sci.)	
Coolant gas flow rate	16 L/min
Auxiliary gas flow rate	0.80 L/min
RF power	1264 W
Mass window	10%
Time per pass	2.0 s
Resolution	Medium resolution ($\Delta m/m = 8000$: FWHM)

[a] Operating parameters for the analysis of Nodule-A.
[b] Operating parameters for Nodule-B.