Comparison of 265 nm Femtosecond and 213 nm Nanosecond Laser Ablation Inductively Coupled Plasma Mass Spectrometry for Pb Isotope Ratio Measurements

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The analytical performance of 265 nm femtosecond laser ablation (fs-LA) and 213 nm nanosecond laser ablation (ns-LA) systems coupled with multi-collector inductively coupled plasma mass spectrometry (MC-ICPMS) for Pb isotope ratio measurements of solder were compared. Although the time-resolved signals of Pb measured by fs-LA-MC-ICPMS showed smoother signals compared to those obtained by ns-LA-MC-ICPMS, similar precisions on Pb isotope ratio measurements were obtained between them, even though their operating conditions were slightly different. The mass bias correction of the Pb isotope ratio measurement was carried out by a comparison method using a Pb standard solution prepared from NIST SRM 981 Pb metal isotopic standard, which was introduced into the ICP by a desolvation nebulizer (DSN) via a dual-sample introduction system, and it was successfully demonstrated for Pb isotope ratio measurements for either NIST 981 metal isotopic standard or solder by fs-LA-MC-ICPMS since the analytical results agreed well with the certified value as well as the determined value within their standard deviations obtained and the expanded uncertainty of the certified or determined value. The Pb isotope ratios of solder obtained by ns-LA-MC-ICPMS also showed agreement with respect to the determined value within their standard deviations and expanded uncertainty. From these results, it was evaluated that the mass bias correction applied in the present study was useful and both LA-MC-ICPMS could show similar analytical performance for the Pb isotope ratio microanalysis of metallic samples such as solder.

Keywords 265 nm femtosecond laser ablation (fs-LA), 213 nm nanosecond laser ablation (ns-LA), multi-collector inductively coupled plasma mass spectrometry (MC-ICPMS), LA-MC-ICPMS, Pb isotope ratio measurements, solder

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Introduction

It is well known that Pb is one of the toxic elements and Pb isotopic analysis is useful to evaluate the source of Pb in environmental and biological samples.1–17 The Pb is certainly the most powerful among radiogenic elements available with respect to isotope geochemists, because it has three radiogenic isotopes whose precursors of U and Th are relatively short half-lives and are very different from each other, and the chemistry of Pb is also quite different from that of its precursors. Laser ablation multi-collector inductively coupled plasma mass spectrometry (LA-MC-ICPMS) has already been accepted as a suitable tool for precise isotopic microanalysis in solid samples at scales down to about 5 – 100 μm; since the MC-ICPMS can achieve simultaneous multi-isotope measurements by its multi-collector even though the number of detector is limited. Therefore, LA-MC-ICPMS is considered to be the best instrument for accurate and precise isotopic microanalysis and it has been applied in many fields of research, such as in U-Pb geochronology of zircon, analysis of magmatic melt inclusions and so on.16–31 The current direction concerning the development and advanced researches on laser ablation is femtosecond-LA (fs-LA). It shows better analytical performance form the view of elemental fractionation effects, which show the capability concerning the non-matrix matching calibration method for the quantitative analysis of elements.32 However, the effect could actually be observed on conductive samples such as metals. The fs-LA does not always show better elemental fractionation on non-conducting materials such as glass, since similar elemental fractionation effects were obtained among 193 nm nanosecond-LA (ns-LA), 265 nm fs-LA and 795 nm fs-LA in our previous study.33 From these points of view, the figures of merit should be determined for either fs-LA or ns-LA to explore suitable applications.

The purpose of the present study is the comparison of the analytical performance on Pb isotope ratio measurement between 265 nm fs-LA and 213 nm ns-LA coupled with the MC-ICPMS, in order to figure out the benefits between them. It is considered that different sizes or different amounts of ablated particles are observed due to different interactions between sample and each LA, which is attributed to different laser properties such as pulse duration, laser pulse energy, and so on.
The ablated particles possibly influence on the isotope ratio analysis since different fluctuations such as different dissociations and ionizations of the particles in ICP can be considered. Therefore, the Pb isotope ratio measurement was carried out to evaluate the basic analytical performance of fs-LA and ns-LA in the present study. The solder was chosen as a conductive sample which was expected to be suitable one for the fs-LA, and basic analytical performance of Pb isotope ratio measurement between the fs-LA and the ns-LA was compared by the 208Pb/206Pb isotope ratio because these masses fit to the purpose of the present study due to their higher isotopic abundances compared to that of 204Pb.

**Experimental**

**Instruments**

Figure 1 shows the experimental setup for LA-MC-ICPMS examined in the present study. The operating conditions for the MC-ICPMS and laser ablation systems are also listed in Tables 1 and 2, respectively. The MC-ICPMS used was NuPlasma HR (Nu instruments, UK). The NuPlasma system used has the larger Edwards E2 M80 rotary pump on the sampler/skimmer interface so as to increase the instrumental sensitivity. The fixed collector array of the NuPlasma instrument contains 12 faraday cups, fitted with 1011 ohm resistors and 3 electron multiplier ion counters. Laser ablation was conducted in a He atmosphere and the ablated particulates were swept into the ICP via dual-sample introduction system which was connected between the LA and the MC-ICPMS. As listed in Table 1, a desolvation nebulizer (DSN-100, Nu instruments, UK) was also used and a Pb standard solution for mass bias correction of LA-MC-ICPMS was introduced into the MC-ICPMS via a dual-sample introduction system. For laser ablation, Ti:sapphire fs-LA (Legend, Coherent Inc., Santa Clara, CA) and 213 nm ns-LA (LSX213, Cetac, Germany) were utilized as listed in Table 2. The fs-LA is a chirped pulse amplification (CPA) type of Ti:sapphire based laser system with 150 fs pulse duration. The Ti:sapphire laser was operated at its third harmonic (265 nm). The ns-LA unit was equipped with a 213 nm Nd:YAG laser operating with laser pulse durations of ca. 4 ns, and a homogenizing beam optical system. According to the differences for both the pulse duration and the laser pulse energy of 0.03 mJ for fs-LA and 0.2 or 1.3 mJ for ns-LA, the laser fluencies and irradiances between two lasers were largely different which may result in the different analytical performances on Pb isotope ratio measurement. Since a laser spot size of 100 μm was fixed throughout the present study, the estimated laser fluencies were 0.38 J cm⁻² for fs-LA and 2.5 or 16 J cm⁻² for ns-LA. In the case of fs-LA, the energy hits the sample in a much shorter time; therefore, the laser irradiance is more than 2 orders of magnitude higher than that of the ns-LA as indicated in Table 2. In both cases, the sample was placed in a ca. 30 cm³ ablation cell which was flushed with 1.0 L min⁻¹ He for LA-MC-ICPMS measurements to enhance transport efficiency of the ablated material, and all samples were ablated in a line raster ablation mode. In the case of a mass bias correction, He carrier gas inside the ablation cell without ablated particulates was mixed with an argon and Pb standard solution from DSN via a dual-sample introduction system before entering the MC-ICPMS. During ablation, He carrier gas inside the ablation cell as well as ablated particulates were mixed with argon and a 1% HNO₃ solution from DSN via a dual-sample introduction system before entering the ICP to maintain a stable MC-ICPMS condition for Pb isotope ratio measurements.

**Samples**

Two solders, named solder A and solder B, which were candidate certified reference materials (CRMs) for Pb measurement produced by National Metrology Institute of Japan (NMIJ, Ibaraki, Japan), were used in the present study. These
solders were of the disk form (30 mm diameter, 5 mm thickness) and comprise ca. 96.5% of Sn, ca. 3% of Ag, and ca. 0.5% of Cu. The Pb concentrations of solders A and B were ca. 200 mg kg⁻¹ and ca. 950 mg kg⁻¹, respectively. A standard reference material (SRM) for the Pb isotopic standard (NIST SRM 981, National Institute of Standard and Technology, Gaithersburg, MY)³⁹ consisted of pure Pb metal (ca. 100% Pb) was used as an unknown sample. A ca. 30 ng mL⁻¹ of Pb standard solution was also prepared from NIST SRM 981 Pb metal isotopic standard for a mass bias correction of the Pb isotope ratio measurements as well as the optimization of the operating conditions of the MC-ICPMS instrument. The Pb isotope ratios of solders A and B were determined and used for comparing the analytical performance on Pb isotope ratio measurement between the fs-LA and the ns-LA coupled with MC-ICPMS. The solders were dissolved by acids and measured by MC-ICPMS equipped with a DSN via dual-sample introduction system as listed in Table 1. In order to dissolve the solder, the disk was scraped by a lathe and ca. 0.1 g of the wire form of the solder could be dissolved easily at room temperature by ca. 1 mL of the mixed acid solution consisted of both 31% HNO₃ and 7.6% HF. The dissolved solder solution was further diluted by a mixed acid solution consisted of both 0.2% HNO₃ and 0.1% HF to prepare the solution for measurements.

Mass bias correction for Pb isotope ratio analysis
A mass bias correction for LA-MC-ICPMS in the present study was performed by a comparison method using ca. 30 ng mL⁻¹ of Pb standard solution, because the internal standard method could not be used generally due to its difficulty for the addition of an element standard solution as an internal standard such as Tl for Pb isotope ratio analysis to solid samples such as metals and glasses. Though NIST SRM 981 Pb metallic standard (ca. 100% Pb) is possibly applied for a mass bias correction of Pb isotope ratio measurement of solders (ca. 200 mg kg⁻¹ or ca. 950 mg kg⁻¹ Pb), the Pb standard solution was used since appropriate Pb signals from both NIST SRM 981 and solders could not be obtained under the same operating conditions of each LA due to huge differences of the Pb concentrations between samples. All LA-MC-ICPMS measurements including the mass bias correction were carried out using the time-resolved analysis mode. Each line raster analysis consisted of approximately 60 s background acquisition (gas blank) followed by 120 s laser ablation from the sample.

Results and Discussion

Determination of the ²⁰⁸Pb/²⁰⁶Pb isotope ratio of solder by DSN-MC-ICPMS
The ²⁰⁸Pb/²⁰⁶Pb isotope ratio of solder dissolved was determined by DSN-MC-ICPMS. The ideal mass spectrum is shown in Fig. 2(a) observed for ca. 30 ng mL⁻¹ Pb standard solution. It has been noticed that the flat top-rectangular shape as well as the intensity of the mass spectrum is very important to achieve accurate and precise isotope ratio measurements. The triangle shape of mass spectra was observed for solder A (ca. 200 mg kg⁻¹ Pb) as shown in Fig. 2(b) when the dissolved solution with low dilution factor such as 6000 times was measured by DSN-MC-ICPMS, which was attributed to the distortion of the ion beam of Pb originated from matrix elements of the solder such as Sn (ca. 96.5%), Ag (ca. 3%) and Cu (ca. 0.5%). In order to get rid of any distortion of the ion beam of Pb, further dilution was carried out even though the concentration of Pb became lower. Figure 2(c) shows the mass spectra obtained by a dissolved solution of solder A with more than 75000 times dilution. The flat top-rectangular shaped mass spectra of Pb were successfully obtained and the concentration of Pb and the matrix element of Sn were ca. 2.7 ng g⁻¹ and ca. 13 μg mL⁻¹, respectively. Figure 3 shows the Pb isotope ratios obtained as a function of the dilution factor for a dissolved solution of solder A. The mass bias of the Pb isotope ratio of solder was corrected by the comparison method using the Pb standard solution. As can be seen in Fig. 3, the sample solution with a dilution factor of more than 75000 times showed similar Pb isotope ratios, which indicated successful isotope ratio measurements. Although the matrix elements have an effect on the distortion of the ion beam which disturbs accurate isotope ratio measurements, they can be reduced by dilution if the concentration of the measurand in the sample is sufficiently high after dilution. The ²⁰⁸Pb/²⁰⁶Pb isotope ratios determined for

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Fig. 3 $^{208}$Pb/$^{206}$Pb isotope ratio (○) obtained by DSN-MC-ICPMS and calculated concentration of Sn (□) as a function of the dilution factor of dissolved solder A (ca. 200 mg kg$^{-1}$ of Pb). The bar indicated is standard uncertainty ($k = 1$) estimated for measured Pb isotope ratio. A mass bias correction for each isotope ratio obtained was performed by the comparison method using ca. 30 ng mL$^{-1}$ Pb standard solution prepared from NIST SRM 981 Pb metal isotopic standard. The threshold concentration of Sn was evaluated to be less than 1.3 μg g$^{-1}$ for Pb isotope ratio (dilution factor was more than 75000 times).

Fig. 4 Time-resolved signals of Pb and $^{208}$Pb/$^{206}$Pb isotope ratios observed for either DSN-MC-ICPMS or LA-MC-ICPMS. (a) Pb signal and (b) $^{208}$Pb/$^{206}$Pb isotope ratio for ca. 30 ng mL$^{-1}$ of Pb standard solution prepared from NIST SRM 981 metal isotopic standard obtained by DSN-MC-ICPMS, (c) Pb signal and (d) $^{208}$Pb/$^{206}$Pb isotope ratio for solder B (ca. 950 mg kg$^{-1}$ Pb) obtained by 265 nm fs-LA-MC-ICPMS, (e) Pb signal and (f) $^{208}$Pb/$^{206}$Pb isotope ratio for solder B obtained by 213 nm ns-LA-MC-ICPMS.
solders A and B contained ca. 200 mg kg\(^{-1}\) and ca. 950 mg kg\(^{-1}\) Pb were 2.12967 ± 0.00091 (0.043 %, \(k = 2\)) and 2.13145 ± 0.00085 (0.040 %, \(k = 2\)), respectively.

Comparison of the time-resolved signals of Pb and the Pb isotope ratios between fs-LA and ns-LA coupled with MC-ICPMS

Figures 4(a) – 4(f) show the time-resolved signals of Pb as well as \(^{208}\text{Pb}/^{206}\text{Pb}\) isotope ratios observed for DSN-MC-ICPMS, fs-LA-MC-ICPMS and ns-LA-MC-ICPMS. The integration time set for the time-resolved signal was 0.2 s, which was the default one for the MC-ICPMS. The stable time-resolved signals of Pb and the \(^{208}\text{Pb}/^{206}\text{Pb}\) isotope ratios with small relative standard deviation (RSD, %) of ca. 0.03%, whose ratio was used for the mass bias correction, were obtained by DSN-MC-ICPMS for the Pb standard solution as shown in Figs. 4(a) and 4(b), though the integration time was not sufficiently long for precise isotope ratio measurements. If the integration time and the number of replicates are sufficient, 0.005 – 0.001% of RSD can be obtained for the isotope ratio measurements normally by MC-ICPMS even though the total measurement time becomes longer. The time-resolved signals of Pb as well as \(^{208}\text{Pb}/^{206}\text{Pb}\) isotope ratios observed for solder B obtained by 265 nm fs-LA and 213 nm ns-LA coupled with MC-ICPMS are shown in Figs. 4(c) – 4(f). Since the Pb concentration in solder A (ca. 200 mg kg\(^{-1}\)) was insufficient to evaluate the analytical performance on Pb isotope ratio measurements between fs-LA and ns-LA-MC-ICPMS, solder B (ca. 950 mg kg\(^{-1}\) Pb) was measured. As can be seen in Figs. 4(c) and 4(e), though the smooth and the fluctuated time-resolved signals were observed for the fs-LA and the ns-LA, respectively; similar RSD of 0.05 – 0.06% on Pb isotope ratio measurements were obtained as shown in Figs. 4(d) and 4(f). However, add the RSDs obtained by each LA-MC-ICPMS were ca. 2 fold larger than those of the Pb standard solution obtained by DSN-MC-ICPMS. From these results, it was considered that the ablated particles from LA resulted in the larger fluctuation in ICP than that of the solution on the Pb isotope ratio measurements. As mentioned above, a longer integration time could compensate the precision (RSD) which can be attributed to the fluctuation phenomena in the ICP due to the ablated particulates. Figure 5 shows the \(^{208}\text{Pb}/^{206}\text{Pb}\) isotope ratios obtained by fs-LA-MC-ICPMS for NIST SRM 981 Pb metal isotopic standard as a function of the averaged \(^{208}\text{Pb}\) signal intensity. In order to avoid detector saturation, the fs-LA was operated with 0.03 mJ laser pulse energy at a repetition rate of 1 Hz. Although the operating condition of fs-LA was fixed, the averaged \(^{208}\text{Pb}\) signal intensities changed because of the variation of laser pulse energy and laser spot size. The averaged \(^{208}\text{Pb}\) signal intensity was ca. 2 – 3 V and the Pb isotope ratios obtained showed agreement with the certified value within their standard deviation (SD) and expanded uncertainty. The obtained RSD of Pb isotope ratio...
measurement was 0.06 - 0.10% even though the laser pulse energy and spot size were considered to change during ablation. From these results, it was expected that fs-LA-MC-ICPMS with the mass bias correction using the standard solution from DSN could provide accurate analytical results. Figures 6(a) and 6(b) show 208Pb/206Pb isotope ratios obtained by fs-LA-MC-ICPMS for solder B as a function of the averaged 208Pb signal intensity and the repetition rate of the fs-LA, respectively. The measured Pb isotope ratios showed agreement with the determined value within their SD and expanded uncertainty estimated for the determined value. The obtained RSD for measured Pb isotope ratio was 0.05 – 0.15%. As can be seen in Fig. 6, the averaged signal intensity of ca. 3 V as well as a higher repetition rate of 30 – 50 Hz is appropriate to achieve accurate and precise Pb isotope ratio analysis by fs-LA-MC-ICPMS. Figure 7 shows the 208Pb/206Pb isotope ratios obtained by ns-LA-MC-ICPMS for solder B. The measured Pb isotope ratios also showed agreement with the determined value within their SD and expanded uncertainty. A similar RSD of 0.07 – 0.15% was obtained by ns-LA compared to that of fs-LA. The higher averaged signal intensity as well as higher repetition rate showed smaller SD; however, the Pb isotope ratio which was obtained at 20 Hz of repetition rate (ca. 5 V of averaged 208Pb signal intensity) revealed a slight deviation from the determined value even though the obtained results still agreed with the determined value within both the SD and the expanded uncertainty. The averaged signal of ca. 1 – 3 V, which corresponded to the repetition rate of 5 – 10 Hz at 0.2 mJ laser pulse energy for ns-LA, was considered to be appropriate for accurate and precise Pb isotope ratio analysis by ns-LA-MC-ICPMS. The different particle size or different amount of particles generated between the ns-LA and the fs-LA, which could lead the different fluctuation phenomena in the ICP compared to the standard solution introduced from DSN, might be the reason for the deviation observed for higher averaged signal intensity of ca. 5 V as well as higher repetition rate of 20 Hz for ns-LA-MC-ICPMS. The distortion of the ion beam could be considered as the reason for the deviation. From these results, the operating conditions of both LA-MC-ICPMS which provided the averaged 208Pb signal intensity of ca. 2 – 3 V were considered to be appropriate for Pb isotope ratio analysis demonstrated in the present study.

Conclusions

The analytical performance on Pb isotope ratio measurement between the fs-LA and the ns-LA coupled with MC-ICPMS was compared in the present study. The mass bias correction of Pb isotope ratio measurement by the comparison method using Pb standard solution introduced into MC-ICPMS from DSN via a dual-sample introduction system, which could also provide the optimization of the instrument conveniently, was successfully demonstrated for accurate Pb isotope ratio measurements for either fs-LA-MC-ICPMS or ns-LA-MC-ICPMS. The analytical performance was similar to each LA-MC-ICPMS under appropriate operating condition. Although RSD of 0.05 - 0.15% was observed for both LA-MC-ICPMS, the precision could be improved by extending the integration time of MC-ICPMS. From these results, the mass bias correction used in the present study and both LA-MC-ICPMS with appropriate operating conditions could provide accurate Pb isotope ratio analysis of metallic samples such as solder.

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