JAAS

TECHNICAL NOTE

View Article Online
View Journal | View Issue

Cite this: J. Anal. At. Spectrom., 2017, 32, 686

In situ $^{207}Pb/^{206}Pb$ isotope ratio measurements using two Daly detectors equipped on an ICP-mass spectrometer

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The simultaneous detection of ^{206}Pb and ^{207}Pb ions has been made by multiple-ion counting ICP-mass spectrometry using two Daly detectors (MC-ICPMS). To evaluate the long-term gain stability of the detectors, $^{135}Ba/^{138}Ba$ and $^{136}Ba/^{138}Ba$ ratios have been measured by a combination of Daly and Faraday detectors ($^{135}Ba(D)/^{138}Ba(F)$) and an electron multiplier and Faraday detectors ($^{136}Ba(EM)/^{138}Ba(F)$). The measured $^{136}Ba(EM)/^{138}Ba(F)$ ratio changed 2% through the 10-hour analysis, whereas the $^{135}Ba(D)/^{138}Ba(F)$ showed smaller changes (<0.5%) over the 10-hour period, demonstrating that the Daly detector could provide better gain stability against conventional electron multipliers. After the correction for the counting loss due to dead time, the Daly detector is capable of accepting signal intensities as high as 10^7 cps. This indicates that the overlap of the analysis range, between the Daly detector (10^0 to 10^7 cps) and the Faraday detector (10^4 to 10^{10} cps), would be at least two orders of magnitude, suggestive of easier cross calibration of the collector gain between the detectors. With the present two Daly detectors, *in situ* $^{207}Pb/^{206}Pb$ ratio measurements have been made on the Nancy 91500 zircon standard through the sample introduction technique using laser ablation. The overall analytical precision and the relative deviation from the literature values were 5.1% and 0.04%, respectively. The data obtained here clearly demonstrate that the LA-MC-ICPMS technique equipped with the Daly detectors would become a major analytical tool for *in situ* U–Pb geochronology.

Received 12th August 2016
Accepted 20th January 2017

DOI: 10.1039/c6ja00291a

rsc.li/jaas

1. Introduction

Lead isotope signature has been widely used to define the age of the geochemical samples and also used to trace the origin of rocks, airborne dust, or archeological materials.[1–3] Many geochemists are increasingly interested in the *in situ* Pb isotope data from the specific area of minerals or solid materials to minimise the contribution of Pb from the environment, secondary phases and/or minerals. To achieve this, several probing techniques, such as secondary ion mass spectrometry (SIMS), electron-probe micro-analyser (EPMA), or laser ablation-ICP-mass spectrometry (LA-ICPMS) have been adopted.[4–7] Among these, the LA-ICPMS technique is likely to become a method of choice for geochemists because of simple sample preparation, high-sensitivity and susceptibility to the non-spectral interferences.

In the last few decades, the resulting spatial resolution for the *in situ* isotope ratio measurements has been dramatically improved by increasing the elemental sensitivity of the ICPMS instruments. Moreover, a multiple collector system coupled to the ICPMS technique (MC-ICPMS) provided both the further higher precision and the better spatial resolution of the *in situ* Pb isotope ratio measurements,[8–12] and thus the LA-ICPMS technique has become one of the principal choices for *in situ* Pb isotope ratio measurements.

Despite the obvious success in obtaining high precision Pb isotope ratio data, with the conventional multiple collection using the Faraday detectors, the measured Pb isotope ratio data can be erroneous when the signal intensities of the analytes are unstable. Deterioration in both the precision and accuracy of the isotope ratio measurements can be due to the slow response of the Faraday amplifier.[13,14] Contribution of the slow response of the amplifier was greater when the laser ablation sampling technique was adopted. The resulting signal intensity profile could be unstable, because of time-dependent changes in the amount of laser-induced sample aerosols, and also because of the introduction of large-sized sample particles into the ICP.[15,16] To overcome this, a signal smoothing device was widely applied to improve the precision of the isotope ratio measurements.[17,18] Moreover, Faraday detectors equipped with a fast-response

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amplifier system were developed to minimise the contribution of changes in the signal intensities.[19–21] With the fast-response amplifiers using 10^{12} to 10^{13} ohm resistors, both the downsizing of the sample and the better precision in the Pb isotope ratio measurements can be achieved. Despite this, data reported by Kimura *et al.*[19] revealed that the Faraday amplifiers utilizing 10^{12} to 10^{13} ohm resistors might not be fast enough to follow changes in the signal intensity, and thus, the stability of the signal intensity profile was still a key issue to derive the best precision and accuracy in the isotope ratio data.

With the ion-counting technique utilising an electron multiplier (EM), much faster response can be achieved, and therefore, the multiple ion detectors using the EMs would be the most suitable ion-detection system for the isotope ratio measurements under the unstable or transient signals, likely the case found in the laser ablation analysis.[22–24] The major problem associated with the high-gain ion detector, including the EMs, would be the time-dependent changes in the gain of the ion detector during the analysis (*i.e.*, aging).[25–27] To minimise the contribution of detector aging,[28] isotopic ratio measurements must be carried out using the signal intensities for analytes being within the proper range (*e.g.*, $<5 \times 10^5$ cps).

A wider dynamic range of the ion collector is still a key issue to obtain reliable isotope ratio data from the analytes. For Pb isotope ratios on young zircons (*e.g.*, younger than 1 Ma), the $^{206}Pb/^{238}U$ and $^{207}Pb/^{235}U$ ratios can become <0.0001. This means that the resulting signal intensity of ^{238}U can exceed 1 000 000 cps under the instrumental conditions that produce a signal intensity of ^{206}Pb >100 cps, and therefore, great care must be given to the systematical error in the measured $^{206}Pb/^{238}U$ and $^{207}Pb/^{235}U$ ratios due to both the lack of detector linearity and the incomplete correction for the counting loss. Faced with this problem, Sakata *et al.*[6,29] employed an attenuator device for the ion detector. With the attenuator device, signal intensities of the monitoring isotopes can be reduced down to a 1/500 level, and therefore, ion signals of greater than 10^7 to 10^8 cps can be monitored. With the attenuator device, the precise U–Pb age data can be derived from very young zircons (<0.5 Ma). However, it should be noted that the contribution of the counting statistics after the signal attenuation becomes greater than that without the attenuation, and therefore, direct detection of high intensity signals would be desired for further precise U–Pb age determinations. In this study, we will demonstrate the unique feature of the multiple-ion counting system using two Daly detectors for the *in situ* isotope ratio measurements.

2. Experimental section

The MC-ICPMS system used in this study was a Nu Plasma II multiple collector-ICP-mass spectrometer (Nu Instruments, Wrexham, UK). The mass spectrometer achieves 520 mm dispersion and incorporates 16 Faraday detectors equipped with amplifiers using 10^{11} ohm feedback resistors. To achieve precise isotope ratio measurements from small samples, a multiple-ion counting system using four high-gain electron multipliers and two Daly detectors was applied. For the zircon U–Pb dating, ^{202}Hg, ^{204}(Hg + Pb), ^{206}Pb, ^{207}Pb, ^{208}Pb, ^{232}Th and ^{238}U ions could be monitored at the same time without mass-scanning either by changing the magnetic or electrostatic fields. Conventional full-size electron multipliers (ETP model 14144, SGE Analytical Sciences, Australia) were used for the detection of ^{202}Hg, ^{204}(Hg + Pb), ^{208}Pb, and ^{238}U ions. For the detection of ^{206}Pb and ^{207}Pb ions, two Daly collectors were adopted. The Daly detector has been widely applied for the elemental and isotopic analyses for small-sized samples using TIMS, Noble Gas MS, Glow Discharge MS, or ICP-MS techniques.[23,30] The Daly detector was basically applied for single collector-based instruments, because of the large-physical size of the Daly detector. In this study, a series of ion deflectors was applied to achieve wider mass dispersion among the isotopes, and thus the simultaneous detection of two ion signals using the two Daly detectors (Fig. 1). Voltages of ion transfer lenses, ion deflectors, and the Daly knobs were tuned to maximize the signal intensity and also to achieve the peak flatness of the

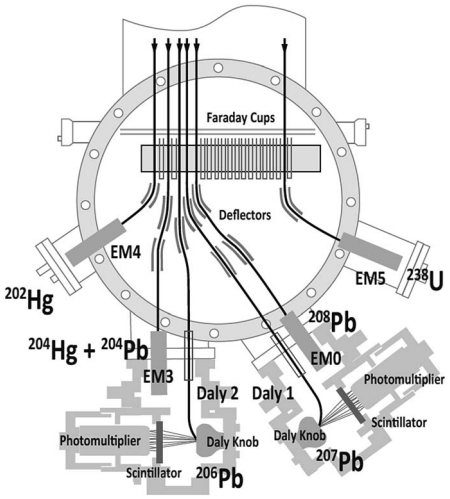

Fig. 1 Schematic diagram of collector arrangements.

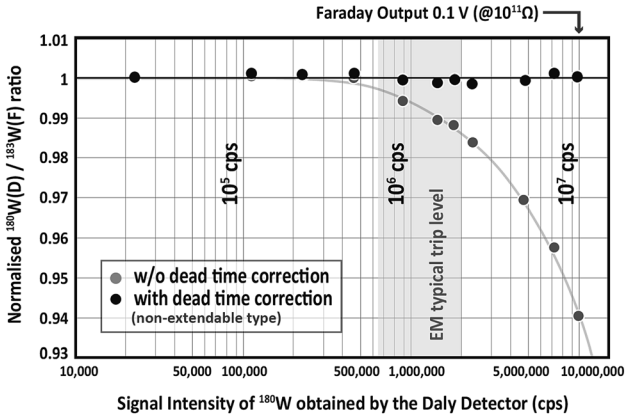

Fig. 2 Measured $^{180}W(D)/^{183}W(F)$ ratio with and without the correction of the counting loss due to the dead time. The gray circles denote the measured signal intensity data without the correction of the dead time, and the black solid circles represent the data after the correction based on the non-extendable model.

analytes. Hence, the identical voltages of −22 kV were applied for both knobs for the Daly 1 and Daly 2 detectors, and the resulting ion detection yield was better than 85%.

The dead times of the two Daly detectors were calculated through the changes in the measured $^{180}W/^{183}W$ ratio obtained by the solution nebulisation of W standard solutions of various concentrations. Intensities of ^{180}W (isotopic abundance = 0.12%) and ^{183}W (isotopic abundance = 14.28%) ions were detected simultaneously using the Daly and Faraday detectors, respectively, and the dependence of the measured $^{180}W/^{183}W$ ratios on the signal intensity of ^{183}W was monitored. The measured W isotope ratios were plotted against the signal intensity of ^{180}W obtained by the Daly detector (Fig. 2). Hence, the measured $^{180}W/^{183}W$ ratios were normalised by the averaged $^{180}W/^{183}W$ ratio calculated from the ratio data obtained with the signal intensity of ^{180}W being 10 000–500 000 cps. Without the correction for the counting loss due to the dead time, the measured $^{180}W(D)/^{183}W(F)$ ratio changed significantly when the signal intensity exceeded 500 000 cps. The calculated dead times for the Daly 1 and Daly 2 collectors were 6.5 ± 0.5 ns and 8.0 ± 0.8 ns, respectively. Hence, the conventional non-extendable model was adopted to calculate the dead time.[26,31] After the proper correction for the counting loss, there were no systematical changes in the measured $^{180}W(D)/^{183}W(F)$ data (Fig. 2).

The laser ablation system used in this study was the ESI NWR193 laser ablation system utilising an ArF Excimer laser (ESI New Wave Research, Oregon, USA). Operational conditions, such as the ablation pit size, repetition rates, or fluence (J cm^{-2}) were tuned to provide a stable signal intensity profile and minimum contribution of signal spikes, caused by the release of large-sized sample particles from the sample. Hence, a fluence of about 3.0 J cm^{-2} and a repetition rate of 2 Hz were employed for the $^{207}Pb/^{206}Pb$ ratio measurements. The details of the instrumentation and operational settings are summarized in Table 1.

Table 1 Instrumentation and operational settings

(a) Laser ablation system	
Instrument	NWR 193 (ESI New Wave Research, Portland, USA)
Cell type	Two volume cell
Wavelength	193 nm
Fluence	3.0 J cm^{-2}
Repetition rate	2 Hz
Ablation pit size	10 μm
Sampling mode	Single hole drilling
Pre-cleaning	2 shots cleaning
Carrier gas	He gas and Ar make-up gas combined outside ablation cell
He gas flow rate	0.54 L min^{-1}
Ar make-up gas flow rate	0.94 L min^{-1}
Number of shots	20 shots per spot
(b) MC-ICP mass spectrometer	
Instrument	Nu Plasma II MC-ICPMS (Nu Instruments, Wrexham, UK)
RF power	1300 W
Interface	Sampler: dry cone Skimmer: HS1 dry skimmer cone
Detection mode	Static mode
Monitored isotopes	^{202}Hg, ^{204}(Hg + Pb), ^{206}Pb, ^{207}Pb, ^{208}Pb, ^{232}Th, ^{235}U
Integration time per spot	8 s
Data reduction	Preablation of 1 s was adopted (signal intensity data for the first 1 s was not used for calculations), because of the possible contribution of the signal spikes caused by the introduction of large-sized particles into ICP
Detectors	
Full size electron multiplier	^{202}Hg, ^{204}(Hg + Pb), ^{208}Pb, ^{235}U
Daly detector	^{206}Pb, ^{207}Pb
Faraday detector	^{232}Th
(c) Corrections of gain and mass bias for $^{207}Pb/^{206}Pb$ ratio measurements	
Gain and bias correction	NIST SRM610
Normalisation Value	$^{207}Pb/^{206}Pb$ = 0.90978 (ref. 9)

3. Results and discussion

3.1 Gain stability

With the multiple-ion counting system setup, the time-dependent changes in the gain of the ion detector can cause a systematical error in the measured isotope ratios. To test the stability of the gain, the $^{135}Ba(D)/^{138}Ba(F)$ ratio was monitored for over a 10-hour period. For comparison, the $^{136}Ba/^{138}Ba$ ratio was also measured using the combination of a conventional electron multiplier and Faraday detectors ($^{136}Ba(EM)/^{138}Ba(F)$). Hence, the solution nebulization technique was used to obtain stable Ba isotope signals over the 10 hours. The Ba analysis solution was prepared through the dilution of the commercially available AA standard solution (Kanto Chemicals, Tokyo, Japan) with 0.2% HNO_3. Concentration of Ba in the analysis solution was about 0.1 μg L^{-1}, and the resulting signal intensities were about 100 000 cps for ^{135}Ba and ^{136}Ba and about 0.01 V for ^{138}Ba. It should be noted that the Ba ions (10^5 cps) continuously struck the EM and Daly detectors for 10 hours. The measured $^{135}Ba(D)/^{138}Ba(F)$ and $^{136}Ba(EM)/^{138}Ba(F)$ were plotted against the run time (Fig. 3). In this figure, the $^{135}Ba/^{138}Ba$ and $^{135}Ba/^{138}Ba$ ratio values were normalised by the initial values calculated from the first 10 minutes. The measured $^{136}Ba(EM)/^{138}Ba(F)$ ratio became lower (about 2%) through the

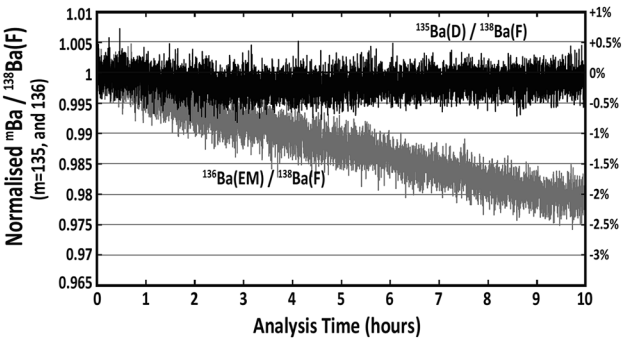

Fig. 3 Normalised $^{136}BA(EM)/^{138}BA(F)$ and $^{135}Ba(D)/^{138}BA(F)$ ratios plotted against the analysis time.

analysis time over 10 hours (Fig. 3). In contrast, the relative deviation of the measured ^{135}Ba(D)/^{138}Ba(F) ratio from the initial values was 0.5% or smaller (Fig. 3), demonstrating that the Daly detector provided better medium- to long-term gain stability.

3.2 Correction for the counting loss

The counting loss mainly originates from an injection of multiple ions into the detector within the indistinguishable time interval. The correction of the counting loss is very important to obtain reliable isotope data. For most ion-counting techniques, correction of the counting loss for the ions has been made based on the non-extendable model.[26,30] However, it should be noted that the counting loss of ions could not be corrected only by the conventional non-extendable model. Richter *et al.*[32] reported that the measured ^{238}U/^{235}U changed linearly up to a 5‰ level on increasing the ion counts (*i.e.*, >10^5 cps). This is mainly due to the contribution of the counting loss of only ^{238}U ions. However, it should be noted that the linear correlation of the measured isotope ratio and the signal intensities found in the ^{238}U/^{235}U measurement could not be corrected by both non-extendable and extendable models for the counting loss.[33–35] This suggests that the loss of signal-output linearity was not only caused by the overlapping of the timing of ion entry into the detector, but also by gain deterioration.[25,26,28,31]

Fig. 2 illustrates the normalised ^{180}W(D)/^{183}W(F) ratio plotted against the signal intensity of ^{180}W. After the proper correction for the counting loss due to the dead time, no significant changes in the measured ^{180}W(D)/^{183}W(F) ratio could be found. Hence, the correction for the counting loss was based on the conventional non-extendable model. This suggests that the counting loss found in the Daly detector mainly originates from the overlapping of the timing of the ion entry into the detector, and thus, the contribution of gain deterioration could be negligibly small. More importantly, data points found in the Fig. 2 clearly demonstrate that the Daly detector was capable of accepting very high count rate signals (>10^7 cps). The count rate of 10^7 cps is equivalent to the signal output of about 0.16 V on the Faraday detectors, equipped with a 10^{11} ohm negative feedback resistor for the amplification. This indicates that the overlaps for the measurable range of the signals exceeds by at least 2 orders of magnitude between the Daly and Faraday detectors, demonstrative of easier cross calibration for these detectors.

3.3 Pb isotope ratio

To demonstrate the analytical capability of the present two Daly detectors, we have measured the ^{207}Pb(D1)/^{206}Pb(D2) ratio for the Nancy 91500 natural zircons using a laser ablation sampling technique. The ablation pit size of 10 μm, a repetition rate of 2 Hz, a fluence of 3.0 J cm^{-2} and a signal integration time of 8 s were adopted for the isotope ratio measurements. The typical depth of the ablation pit after the laser ablation was <5 μm. The isotope ratio measurements were repeated 15 times by the laser ablation of separated 15 ablation pits. Both the gain and mass bias factors were corrected by normalising the ^{207}Pb/^{206}Pb ratio for NIST SRM610 being 0.90978 (Jochum *et al.*[9]). The resulting ^{207}Pb(D2)/^{206}Pb(D1) ratios obtained from 15 repeated measurements are given in Table 2. The analytical precision defined by 2δ standard deviation from 15 repeated measurements was about 5%. The resulting ^{207}Pb/^{206}Pb was 0.07485 ± 0.0038 (2δ, n = 15), and this agreed well with the literature values (0.07488; Wiedenbeck *et al.*[36]) within the analytical uncertainties, suggesting that the reliable isotope ratio data can be made even under the unstable signal intensity profile obtained by the laser ablation sampling technique. Both the simple correction for the counting loss and the better gain stability were achieved by the Daly ion detectors. The isotope ratio data obtained here demonstrate that the Daly detector would be the principal choice for the ion collector for the *in situ* isotope ratio measurements from small sample sizes.

Table 2 Measured ^{207}Pb/^{206}Pb isotope ratio for the Nancy 91500 natural zircons obtained by the LA-MC-ICPMS technique

Run	^{207}Pb (D1)/^{206}Pb (D2)
1	0.07714
2	0.07751
3	0.07682
4	0.07408
5	0.07558
6	0.07166
7	0.07323
8	0.07260
9	0.07739
10	0.07432
11	0.07431
12	0.07687
13	0.07332
14	0.07476
15	0.07316
Mean	**0.07485**
2SD	**±0.0038 (5.1%)**
Literature[a]	**0.07488**
% RSD	***−0.041***

[a] Wiedenbeck *et al.* (1995).[36]

4. Conclusions

In this study, Pb isotope ratios have been measured by the laser ablation-MC-ICPMS system equipped with a high-gain electron multiplier and two Daly detectors. The Pb isotopes were simultaneously detected by a multiple-ion counting (MIC) system using full-sized ion multipliers[24] and two Daly detectors. One of the most important features obtained by the Daly ion detectors would be the better long-term gain stability against the conventional electron multipliers.

Another unique feature achieved by the Daly ion detectors was the wide dynamic range. After the correction of the counting loss of the signal due to the dead time, the Daly ion collector is capable of measuring an ion beam size of greater than 10^7 cps. The overlap of the range of the measurable beam size between the Daly and Faraday detectors was at least 2 orders of magnitude, suggestive of easier cross gain calibration between the Daly and Faraday detectors.

To demonstrate the capability of the two Daly detectors, we have measured the $^{207}Pb(D1)/^{206}Pb(D2)$ ratio for the Nancy 91500 natural zircons. The resulting analytical precision in the $^{207}Pb/^{206}Pb$ ratio measurements was about 5%. The measured $^{207}Pb/^{206}Pb$ was 0.07485 ± 0.0038 (2δ, $n = 15$), and the relative deviation from the literature values (0.07488; Wiedenbeck *et al.*[36]) was about 0.04%, suggesting that the reliable isotope ratio data can be achieved from the unstable signal intensity profile obtained by the laser ablation sampling technique. The data exhibited here clearly demonstrate that the multiple-Daly detectors can become effective tools for the U–Pb isotope ratio measurements from small sample sizes.

Acknowledgements

The authors thank Dr H. Iwano and T. Danhara (Kyoto Fission Track, Japan); R. W. Nesbitt and A. Milton (University of Southampton, UK); and D. Günther (ETH, Switzerland) for offering valuable scientific advice. We are also grateful to Dr P. Freedman, A. Burrow and I. Bowen (Nu Instruments, UK) for technical support. This work was partly supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Culture, Sports, Science and Technology, Japan for TH (A26247094).

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