nu plasma II

MULTI COLLECTOR ICP-MS

DETERMINATION OF CERIUM ISOTOPE RATIOS USING A HIGH-GAIN DETECTION SYSTEM

Radiogenic $^{138}Ce/^{136}Ce$ ratios help constrain the ancient history of light REE enrichment and depletion in Earth and planetary materials, and may also be used for geochronology as ^{138}Ce is the daughter product of ^{138}La. However, measurements of $^{138}Ce/^{136}Ce$ ratios are challenging because of (1) the small variations in nature (2) the relative low abundances of both ^{136}Ce and ^{138}Ce (<0.25%) and (3) the significant isobaric interferences on both isotopes. Measurement of Ce as an oxide species by TIMS has yielded precise and accurate $^{138}Ce/^{136}Ce$ ratios [1]. MC-ICP-MS holds considerable promise due to the higher ionization efficiency for Ce and the potential for higher sample throughput. To date, however, the difficulty of correcting for (1) the larger interferences on Ce isotopes using the ICP source (due to its high ionization efficiency for all elements, and the additional presence of interfering ^{136}Xe in the Ar plasma gas) and (2) tailing of the large ^{140}Ce beam under ^{138}Ce has prevented this technique from achieving a level of accuracy and precision that is similar to TIMS [1].

This study demonstrates the development of $^{138}Ce/^{136}Ce$ measurement on the Nu Plasma II MC-ICP-MS using a high-gain detection system.

Fig 1: Nu Plasma II in operation

Repeat analyses were made on a 500 ppb NIST3110 Ce solution, and a 500 ppb SHELF Ce solution, using a Nu Plasma II instrument in Wrexham (Fig. 1). Solution was introduced in 2% nitric acid, using an Aridus-II Desolvating Nebuliser System, with a 90 µL/min glass concentric nebuliser, and the Enhanced Sensitivity interface.

Data was collected using dynamic analysis, each analysis containing 2 blocks of 50 integrations. One integration consisted of a 10 second on-peak measurement of Ce and interfering isotopes in cycle 1, followed by a 2 second measurement of ^{131}Xe in cycle 2 and ^{129}Xe in cycle 3 (Table 1). Zeros were measured by a 120 second ESA deflection at the beginning of each block. Each analysis lasted ca. 78 minutes. No tuning of the instrument or the Aridus-II was made once the measurement sequence had started.

^{131}Xe, ^{135}Ba, ^{139}La, ^{145}Nd were simultaneously monitored during the course of measurement to correct for the irresolvable isobaric interferences of ^{136}Xe and ^{136}Ba on ^{136}Ce, ^{138}Ba and ^{138}La on ^{138}Ce, ^{142}Nd on ^{142}Ce (Table 1).

Table 1: Cup configuration of Ce isotope measurement on the Nu Plasma II. Grey represents Faraday collectors, green ion counter, yellow dummy bucket. Interfering isotopes are in red.

Collector	H7	X	H6	H5	H4	H3	H2	H1	Ax	L1	L2	L3	L4	IC0	L5
Cycle 1	^{145}Nd		^{142}Nd ^{142}Ce		^{140}Ce	^{139}La		^{138}La ^{138}Ce ^{138}Ba		^{136}Xe ^{136}Ce ^{136}Ba	^{135}Ba				^{131}Xe
Cycle 2														^{131}Xe	
Cycle 3														^{129}Xe	

As is shown in the magnet scan (Fig. 2), Ba and Xe present major isobaric interferences on Ce isotopes. To minimize any error propagation of the ^{136}Xe, ^{136}Ba and ^{138}Ba corrections, ^{135}Ba and ^{131}Xe were both measured on a Faraday collector connected to a pre-amplifier fitted with a 10^{12} ohm resistor, to increase the signal to noise ratio and reduce the measurement uncertainty.

Due to its high abundance, ^{140}Ce was measured on a Faraday collector using a 10^{10} ohm resistor. An internal normalisation to $^{136}Ce/^{142}Ce = 0.01688$ was used for Ce mass fractionation correction. In addition, ^{131}Xe and ^{129}Xe were sequentially monitored on an ion counter to calculate the Xe fractionation, as an inaccurate estimation of Xe isotope composition is found to result in inaccurate $^{138}Ce/^{136}Ce$ ratios.

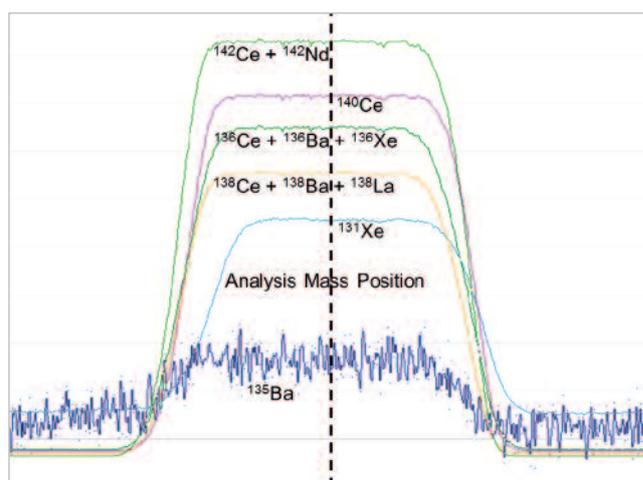Fig 2: Ce and ^{131}Xe, ^{135}Ba peaks in coincidence. The center of the flat peaks was chosen as the analysis mass position.

nu instruments

MULTI COLLECTOR ICP-MS

The achieved Ce sensitivity was approx. 650 volts/ppm. Typical internal precision of the corrected $^{138}Ce/^{136}Ce$ was better than 0.020‰ (2RSE).

The significant low-mass tailing of the ^{140}Ce peak with the Nu Plasma HR instrument [1] has not been observed in this study. This might be attributed to the improved abundance sensitivity of the Nu Plasma II. Therefore, no tail correction was applied to the results of this study.

As is shown in Fig. 3, repeat analyses of the NIST3110 standard over 4 days yielded $^{138}Ce/^{136}Ce$ = 1.33740 ± 0.00005 (2SD, n = 20). This is well in agreement with the reported TIMS result of 1.33738 ± 0.00003 (2SD, n = 34). To validate the necessity of measuring Xe fractionations, the data was re-processed assuming the same fractionation factor for Xe and Ce, resulting in an inaccurate $^{138}Ce/^{136}Ce$ ratio shifted by ~1SD.
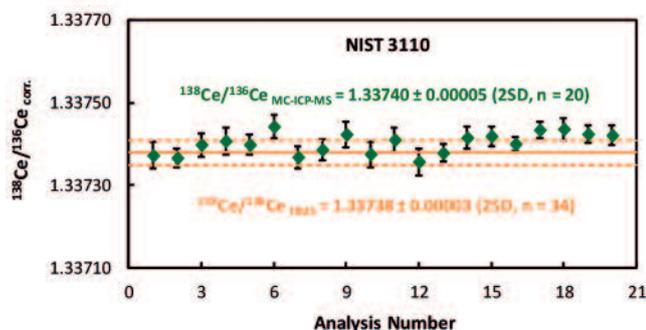

Fig 3: Repeat analyses of a 500 ppb NIST3110 standard solution over 4 days. The result (green diamonds) is in good agreement with the previously reported TIMS result (orange lines) measured on Ce oxides with a tail correction. Error bars are 2SE.

$^{138}Ce/^{136}Ce$ data obtained to date using different analytical methods are compared in Table 2. The TIMS oxide-based approach with a tail correction provides the best precision. The MC-ICP-MS data presented in this study demonstrates the best precision and accuracy for element-based methods.

Table 2: Comparison of the $^{138}Ce/^{136}Ce$ obtained using different analytical approaches (Data source: Willbold, 2007).

Method	$^{138}Ce/^{136}Ce$	2RSD (‰)	n
TIMS oxide-based	1.33746	0.090	34
TIMS oxide-based tail corrected [1]	1.33738	0.023	34
TIMS element based [1]	1.33742	0.354	24
TIMS element-based tail corrected [1]	1.33733	0.335	24
MC-ICP-MS	1.33758	0.733	21
This Study	1.33740	0.038	20

The log-log plot (Fig. 4) of uncorrected $^{138}Ce/^{136}Ce$ versus uncorrected $^{136}Ce/^{142}Ce$ displays a perfect linear correlation (R^2 = 0.9917) with a slope within errors of the theoretical value of -0.33. This confirms the suitability of the exponential law for the mass fractionation correction in this study.
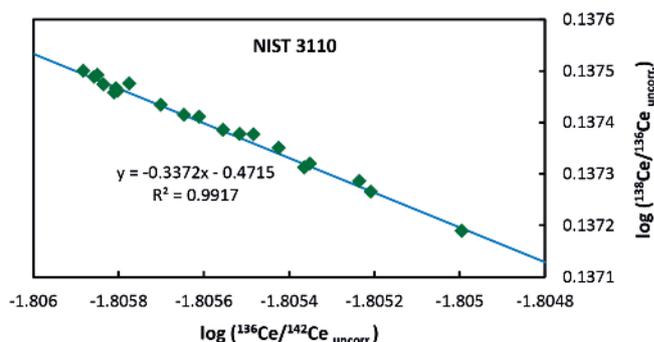

Fig 4: Log($^{138}Ce/^{136}Ce$ uncorr.) and log($^{136}Ce/^{142}Ce$ uncorr.) display a linear correlation.

Willbold (2007) reported a positive correlation between the corrected $^{138}Ce/^{136}Ce$ ratio and the calculated ^{138}Ba beam intensity, suggesting an insufficient interference correction of ^{138}Ba on ^{138}Ce. In this study, the calculated ^{138}Ba intensity (based on measured ^{135}Ba) is plotted against the corrected $^{138}Ce/^{136}Ce$ ratio in Fig. 5, with no clear correlation found between the two. The measurement of ^{135}Ba using a 10^{12} ohm resistor has evidently reduced the measurement uncertainties and improved the interference corrections.
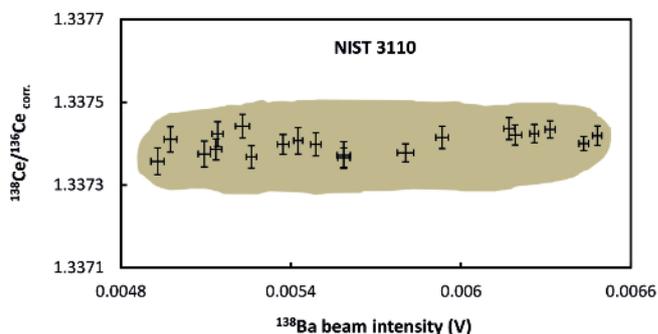

Fig 5: Plot of the corrected $^{138}Ce/^{136}Ce$ versus the calculated ^{138}Ba intensity of the NIST3110 standard solution. Error bars are 2SE.

As a REE element, high levels of oxide formation are often observed on the ICP instruments for Ce isotopes. This is reported to be accompanied by a significant non-linear contribution to the instrumental mass fractionation [2]. Tests performed in this study when the CeO^+/Ce^+ was as high as 1% yielded significantly elevated $^{138}Ce/^{136}Ce$ ratios and poor precisions (Fig. 6). To ensure the validity of the mass fractionation law, the CeO^+/Ce^+ was kept below 0.1% for all measurements.
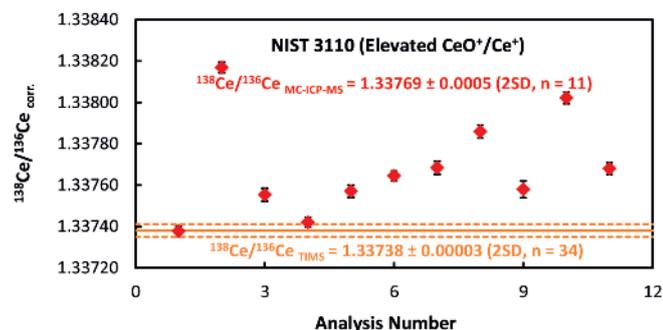
Fig 6: $^{138}Ce/^{136}Ce$ obtained on the 500 ppb NIST3110 solution when CeO^+/Ce^+ = 1% are significantly higher than the TIMS result (orange lines). Error bars are 2SE.

A SHELF Ce standard was analysed in a 13 hour session (Fig. 7). An external reproducibility similar to that of the NIST3110 standard was achieved (2SD = 0.00005).
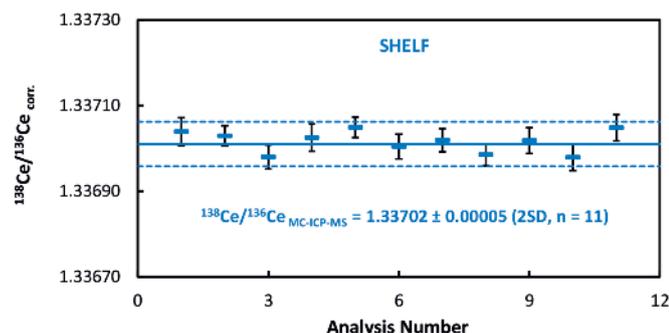

Fig 7: Repeat analyses of a 500 ppb SHELF Ce solution in a 13 hour session. Error bars are 2SE.

Experiments have demonstrated the capability of the Nu Plasma II for precise and accurate Ce isotope measurements using a high gain detection system. The element-based measurements have achieved $^{138}Ce/^{136}Ce$ =1.33740 ± 0.00005 (2SD, n = 20) for the NIST3110 standard without any tail correction, well in agreement with the TIMS reference values [1] and having significantly improved the existing Ce measurements on the MC-ICP-MS.

References

[1] Willbold, 2007. *J. Anal. At. Spectrom.* 22, 1364-1372.

[2] Newman et al., 2009. *J. Anal. At. Spectrom.* 24, 742-751.

Acknowledgements