Front. Chem. China 2008, 3(1): 94–98
DOI 10.1007/s11458-008-0019-y

RESEARCH ARTICLE

Yueheng YANG, Hongfu ZHANG, Liewen XIE, Fuyuan WU

Accurate measurement of neodymium isotopic composition using Neptune MC-ICP-MS

Abstract This paper reports the measurement of the Neodymium isotopic composition by Neptune Multiple Collector Inductively Coupled Plasma Mass Spectrometry (MC-ICP-MS) over the last two years. Although there is concomitant Cerium in the chemical separation process, this has no significant influence on the Neodymium analysis. As for the sample containing small amounts of Samarium ($Sm/Nd < 0.04$), direct calibration for isobaric interference and mass discrimination by the exponential law can be obtained by assuming that Samarium mass discrimination is the same as that of Neodymium. Geological samples after traditional chemical separation were measured by Neptune MC-ICP-MS and Thermal Ionization Mass Spectrometry (TIMS) respectively. The results show that Neptune MC-ICP-MS can measure Neodymium isotopic composition as precisely the TIMS does and is even more effective and less time-consuming than the TIMS Method.

Keywords MC-ICP-MS, neodymium isotopic composition, cerium and Samarium isobaric correction

1 Introduction

Inductively Coupled Plasma Mass Spectrometry (ICP-MS) has become very popular and has been widely used in many fields such as geological, environmental, electronic and medicinal analysis since its first appearance in the 1980s. Multicollector ICP-MS (MC-ICP-MS) just appeared nearly a decade ago. The main advantage of MC-ICP-MS is that it can be used with a magnetic sector multi-collector Faraday cup array and can sustain high temperature. It is also an efficient ICP ion source [1]. Compared with the traditional Thermal Ionization Mass Spectrometry (TIMS), ICP can remarkably improve the ionization efficiency since it reaches 6000–8000 K while the former reaches only about 2000 K and can hardly ionize high potential elements (Hf, W) completely. Also, MC-ICP-MS can measure almost all those isotopic elements including the light, middle and heavy mass elements in the periodic table, such as Li, B, Mg, Cu, Fe, Zn, Hf, W, U and on the others [2]. At the same time, the ion source of TIMS is under vacuum conditions while that of ICP is under atmospheric pressure, which makes it easier and more convenient to change the sampling mode. Equipped with a laser ablation system, in-situ isotope analysis can be realized. Because of the relative stability of MC-ICP-MS's fractionation, it can be more efficient for mass bias (Tl for Pb) and isobaric interference correction (^{87}Rb on ^{87}Sr, ^{144}Sm on ^{144}Nd and ^{176}Lu, ^{176}Yb on ^{176}Hf) [3].

Axiom, Isoprobe, Neptune and Nu MC-ICP-MS has been introduced into our country in the recent years. These are used to develop some innovative research work (Hf, Cu and Zn). On the other hand, It is used to do some conventional isotope analysis (Sr, Nd and Pb). As we all know, classic Nd isotopes are widely used in isotope geochemistry and geochronology. Although there have been many reports covering measurement of Nd isotope composition by P54 [4], Axiom [5], Isoprobe [6–9] and Nu [6] MC-ICP-MS, we still lack data on the measurement of the Neodymium composition by Neptune MC-ICP-MS, This paper introduces some detailed information about this.

Translated from *Chinese Journal of Analytical Chemistry*, 2007, 35(1): 71–74 [译自: 分析化学]

Yueheng YANG (✉), Hongfu ZHANG, Liewen XIE, Fuyuan WU
State Key Laboratory of Lithospheric Evolution, Institute of Geology and Geophysics, Chinese Academy of Sciences, Beijing 100029, China
E-mail: yangyueheng@mail.iggcas.ac.cn

Yueheng YANG
Graduate University of Chinese Academy of Sciences, Beijing 100039, China

2 Experimental

2.1 Instrumentation

Thermal Finnigan Neptune MC-ICPMS has a double focusing capability and has the capability of high mass

resolution measurements in multiple collector mode. Due to the zoom design on ion optical magnification, a large mass dispersion of 810 mm and an increased focal depth is achieved. The maximum distance between the outermost cup positions corresponds to a relative mass range of 17% as described in detail previously [10].

2.2 Reagents and standards

All chemical preparations were conducted on special class 100 benches inside a class 10000 clean room. Milli-Q water (18.2 MΩ cm^{-1}) from Millipore (Elix-Millipore, USA) was used throughout and distilled extra-pure reagents were used in this study. Hydrochloric acid (6 mol/L) was prepared by sub-boiling distillation in a home-made quartz still. Concentrated perchloric acid was obtained by decompressed-distillation. Concentrated nitric and hydrofluoric acid were purified by sub-boiling distillation in a Teflon still. A 200 ppb solution of Merk Nd, La Jolla Nd and GSS Nd were used for monitor and optimization Neptune MC-ICP-MS during analytical sessions. A 100 ppm solution of Ce and Sm obtained from the National Research Center of CRM's of China was gravimetrically diluted with 2% HNO_3 to obtain 10 ppm and 100 ppb Ce and Sm for various Ce/Nd and Sm/Nd ratios in the mimic experiment.

2.3 Methods

2.3.1 Sample digestion and purification

About 150 mg of rock powder was weighed in a 15 mL Savillex™ Teflon screw-up capsule with 2 mL concentrated HF, plus 0.2 mL concentrated $HClO_4$ for a week at approximately 100°C. After cooling, the capsule was opened and evaporated at approximately 180°C. Then, 1 mL of 6 mol/L HCl was added to the residue and dried. This procedure was repeated. The residue was dissolved in 1 mL of 2.5 mol/L HCl and the capsule was sealed on a hot plate at approximately120°C overnight. After cooling, the first stage is purification of the rare earth element (REE) from major and matrix element on a conventional cation exchange column loaded with Bio-Rad AG50W-X12 (5 mL resin bed 200–400 mesh size) resins by elution of 6 mol/L HCl. The second stage is separation of Nd from Sm on P204 (HDEHP) (1 mL resin bed 200–400 mesh) resin by elution of 0.2 mol/l HCl. Then, the Nd fraction was separated into two aliquots, one for TIMS, and the other for Neptune MC-ICP-MS. In most cases, full procedural blanks for this technique were < 50 pg of Nd.

2.3.2 Mass spectrometry

The Nd isotopic data was acquired in static, multi-collector mode with low resolution using nine Faraday collectors and the mass configuration array from 140 to 150 in which interference-free ^{140}Ce and ^{147}Sm were monitored for ^{142}Ce on ^{142}Nd and ^{144}Sm on ^{144}Nd, respectively. Prior to analysis, the collectors were aligned using a tuning solution which contains Ce, Sm and Nd. An aliquot of 200 ppb GSS Nd was used regularly to control the quality and to optimize the operational parameters including the torch position, the Ar flow rate and the ion lens focus to get maximum sensitivity. All instrumental operating parameters are summarized in Table 1.

Table 1 Operating parameters of Nd isotopic measurement by Neptune MC-ICP-MS

component	setting
RF power	1304 W
cooling gas	15.2 L/min
acceleration voltage	10 kV
ion lens	automatic
X-Position	−0.3 mm*
Y-Position	−0.6 mm*
Z-Position	−2.1 mm*
mass resolution	400 (Low)
sampling mode	*ca.*15 min (9Blocks × 10cycles)
integration	8 sec/Cycle
nebulizer 1	micromist PFA nebulizer
uptake rate	~ 50 μL/min
sensitivity on ^{146}Nd	~ 7.5 V/ppm
auxiliary gas	~ 0.8 L/min*
sample gas	~ 0.9 L/min*
nebulizer 2	aridus microcentric
spray chamber	70°C
desolvator	160°C
uptake rate	~ 50 μL/min
sensitivity on ^{146}Nd	~ 35 V/ppm
auxiliary gas	~ 0.6 L/min*
sample gas	~ 1.1 L/min*
Ar sweep gas	~ 6.4 L/min*
N_2	~ 3.1 L/min*

*optimized daily

Before performing the high precision ratio measurement, the Neptune MC-ICP-MS was stabilized for at least one hour under normal conditions. The Nd fractions were re-dissolved with 2% HNO_3 and aspirated into the ICP source using a Micromist PFA nebulizer in free aspiration mode. The intensity of ^{146}Nd usually was 7.5 volts, corresponding to a 200 ppb Nd solution. As for those low-content Nd samples, we usually adopt Cetac Aridus to enhance the signal intensity. Our research shows that after optimizing other parameters, the signal intensity can be enhanced nearly 5 times by slightly adjusting the flux of N_2 and Ar. In this way, low-content Nd samples can be measured efficiently. Each analysis comprised nine blocks and each block consists of ten measurements of 8 seconds integration. Usually, it takes approximately 15 minutes for a single sample run. Prior to data acquisition, the baseline was carried out on half-mass before each measurement. To keep memory effects

to a minimum, the introduction system was cleaned with a 3% HNO_3 solution for approximately 5 minutes prior to each analysis. Analytical solutions are aspirated for 15 seconds to obtain stable signal before starting data acquisition.

3 Results and discussion

Before every measurement, it's necessary to do an on-peak-zeros (OPZ) baseline measurement for the sake of eliminating the effects of the small, persistent quantities of Sm and Nd accumulations from the torch and cones before collecting the data. Data reduction is as follows: Firstly, based on the signal intensity of interference-free ^{140}Ce, we can account Ce's contribution to mass of 142, assuming the mass bias of Ce is the same to that of Nd, which can be obtained from $^{145}Nd/^{146}Nd = 0.482639$. Then, the genuine signal intensity of ^{142}Nd can be obtained using $^{142}Ce/^{140}Ce = 0.125424$ [11]. Secondly, based on the signal intensity of interference-free ^{147}Sm, we can account Sm's contribution to the mass of 144 and 148, assuming the mass bias of Sm is the same to that of Nd, which can be obtained from $^{145}Nd/^{146}Nd = 0.482639$. Then, the genuine signal intensity of ^{144}Nd and ^{148}Nd can be obtained using $^{144}Sm/^{147}Sm = 0.20504$, $^{148}Sm/^{147}Sm = 0.75464$ [11]. Finally, $^{143}Nd/^{144}Nd$ ratios is normalized to $^{146}Nd/^{144}Nd = 0.7219$ for mass bias correction using the exponential law [12].

3.1 Standard solution analysis

We accomplished the measurement of Thermal Finnigan Merck Nd, international standard La Jolla Nd and in-house standard GSS Nd for more than 2 years since the completion of our instrument's installation (Fig. 1). The $^{143}Nd/^{144}Nd$ of Merck Nd is 0.511725 ± 0.000014 (2SD, $N = 38$) (Fig. 1(a)), which is identical to the recommended value, 0.511710–0.511740, within error and is also similar to the Finnigan results, 0.511722 ± 0.000003 (1RSD = 6 ppm). The $^{143}Nd/^{144}Nd$ of international standard La Jolla Nd is 0.511849 ± 0.000014 (2SD, $N = 68$) (Fig. 1(b)), which is, within error, is identical to the 0.511860 ± 0.000012 measurement by classic TIMS. As for our in-house standard GSS Nd, its $^{143}Nd/^{144}Nd$ is 0.511604 ± 0.000018 (2SD, $N = 68$) (Fig. 1(c)). The results show that within the error margins, the Nd standard solution result by Neptune MC-ICP-MS is totally consistent with those of by TIMS. Moreover, its internal precision and lasting stability can be compared to that of TIMS.

3.2 Ce interference

Due to the special similar chemical characteristics between Ce and Nd, it is impossible to separate them totally [13,14] while passing through the ion exchange chromatography.

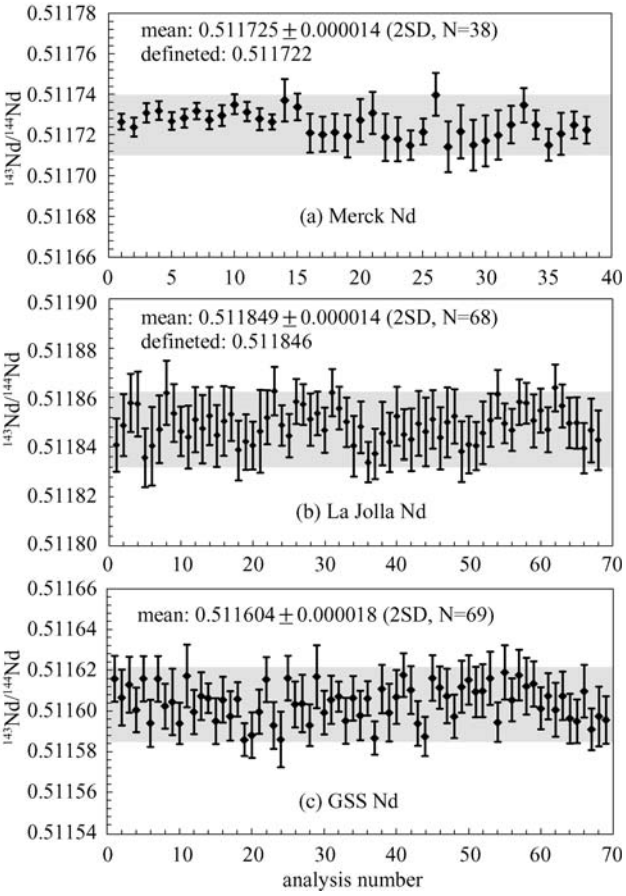

Fig. 1 Variation in analytical results for Merck Nd, La Jolla Nd and GSS Nd by Neptune MC-ICP-MS over two-year period

Gray bands represent 2σ-level reproducibility

We can monitor surviving Ce in the Nd fraction by the signal intensity of interference-free ^{140}Ce. Meanwhile, in order to study if whether a great deal of the Ce that exists will affect Nd isotopic measurement by Neptune, we prepared a series of various Ce/Nd mixed solution (Fig. 2) and the results show that there is no significant influence on the Nd analysis even when Ce/Nd goes up to 3, which is normal in natural geological materials. As a result, even if Ce and Nd have not been separated totally, Ce will not affect the Nd analysis by Neptune. This conclusion has significant implications for in situ Nd measurement by laser ablation MC-ICP-MS. Absolutely different from Isoprobe MC-ICP-MS, when Ce/Nd goes up to 0.1, there will be negative correlations between Ce/Nd and $^{143}Nd/^{144}Nd$ [8]. Although the concrete reason is still unknown at present, it is a Hexapole collision cell for different ion dynamic energy spread and polyatomic interference while electronic static analysis (ESA) is adopted by Neptune.

3.3 Sm interference

The Nd fraction after purification inevitably has small residual Sm content while there is no Sm in standard pure

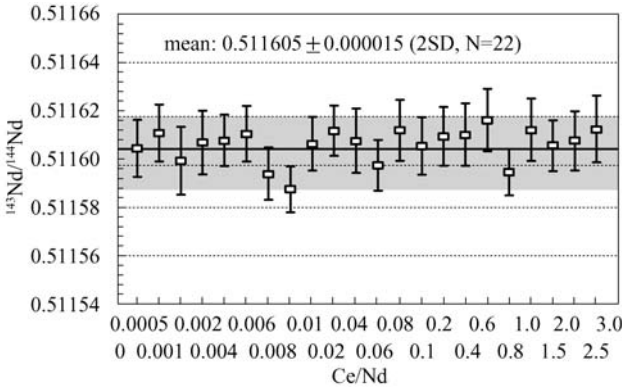

Fig. 2 Results of GSS Nd standard solution with addition of variable Ce content
Gray bands represent 2σ-level reproducibility.

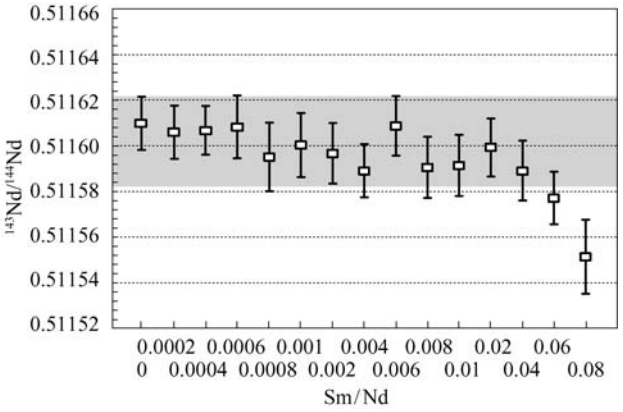

Fig. 3 Results of GSS Nd standard solution with addition of variable Sm content
Gray bands represent the GSS Nd mean valve with 2σ-level reproducibility

Nd solution [13,14]. Generally, there is variable residual Sm in the Nd fraction for natural geogical samples because of its complexity or due to operational errors. Due to the different ionization temperatures, Sm can be burnt off prior to Nd data collection during the traditional TIMS method. As for Nd measured by MC-ICP-MS, due to the high temperature and efficiency of the plasma, Sm and Nd is always ionized at the same time, it is then necessary to consider the interference of Sm and an experiment under the simulated conditions is developed. Therefore GSS Nd solution spiked with various Sm content are measured for our Neptune potential of isobaric interference correction (Fig. 3). The results indicate that direct calibration for isobaric interference and mass discrimination by the exponential law can be obtained by assuming that Sm mass discrimination is the same as that of Nd, even when Sm/Nd goes up to 0.04, which is enough for routine chemical separation.

3.4 Natural geological samples analysis

It is inevitable that the Nd fraction has concomitant matrix or impurities from natural geological samples after the purified protocols described above. Therefore, the natural geological samples are measured in parallel by Neptune MC-IC-MS and TIMS (MAT262) (Table 2). The results indicate that the relative standard deviation between them is always less than 0.006%, which is feasible enough for Nd isotope geochronology and Nd isotope tracer. It demonstrates that Neptune MC-ICP-MS is also suitable for natural geological samples measurement.

4 Conclusions

The measurement of Nd isotopic composition by Neptune MC-ICP-MS is reported in detail in this work. For Nd with concomitant Ce in the purification, there is no significant influence on the Nd analysis in Neptune. As for residual Sm in the purification (Sm/Nd < 0.04), direct calibration for isobaric interference and mass discrimination by the exponential law can be obtained by assuming that Sm mass discrimination is the same as that of Nd. Natural geological samples after traditional chemical separation were measured by Neptune MC-ICP-MS and TIMS, respectively. The results show that Neptune MC-ICP-MS can precisely measure Nd isotopic composition as the TIMS does and is even more effective and less time-consuming than the TIMS method.

Acknowledgements This study was supported by the National Natural Science Foundation of China (Grant No. 40534022).

Table 2 Comparing Nd isotopic data measured by Neptune MC-ICP-MS and TIMS

sample	MC-ICP-MS	TIMS	RSD	sample	MC-ICP-MS	TIMS	RSD
	$^{143}Nd/^{144}Nd$	$^{143}Nd/^{144}Nd$	(%)		$^{143}Nd/^{144}Nd$	$^{143}Nd/^{144}Nd$	(%)
1*	0.512597 ± 0.000011	0.512581 ± 0.000010	0.0031	6	0.512683 ± 0.000010	0.512683 ± 0.000015	−0.0001
2*	0.512336 ± 0.000010	0.512306 ± 0.000010	0.0059	7	0.512515 ± 0.000012	0.512516 ± 0.000010	−0.0002
3*	0.512640 ± 0.000012	0.512639 ± 0.000011	0.0001	8	0.512726 ± 0.000012	0.512738 ± 0.000009	−0.0022
4*	0.512600 ± 0.000011	0.512620 ± 0.000014	−0.0040	9	0.512747 ± 0.000010	0.512749 ± 0.000012	−0.0004
5	0.512648 ± 0.000008	0.512673 ± 0.000010	−0.0049	10	0.512680 ± 0.000012	0.512697 ± 0.000012	−0.0033

*Using Nebulizer 2 and others using Nebulizer 1

References

1. Blichert-Toft J. On the Lu-Hf isotope geochemistry of silicate rocks. Geostandard Newsletters, 2001, 25(1): 41–56
2. Halliday A N, Lee D C, Christensen J N, Walder A J, Freedman P A, Jone C E, Hall C M, Yi W, Teagle D. Recent developments in inductively coupled plasma magnetic sector multiple collector mass spectrometry. International Journal of Mass Spectrometry and Ion Processes, 1995, 146/147: 21–33
3. Halliday A N, Lee D C, Christensen J N, Rehkamper M, Yi W, Luo X, Hall C M, Ballentine C J, Pettke T, Stirling C. Applications of multiple collector ICPMS to cosmochenistry, geochemistry and paleoceansgraphy. Geochimica et Cosmochimica Acta, 1998, 62: 919–940
4. Luais B, Telouk P, Albarede F. Precise and accurate neodymium isotopic measurements by plasma-source mass spectrometry. Geochimica et Cosmochimica Acta, 1997, 61: 4847–4854
5. Gu L B, Shao H X. Determination of isotopic ratio by multi-collector double-focusing inductively coupled plasma mass spectrometry. Journal of Chinese Mass Spectrometry Society, 2004, 25(4): 221–224 (in Chinese)
6. Vance D, Thirlwall M. An assessment of mass discrimination in MC-ICP MS using Nd isotope. Chemical Geology, 2002, 185: 227–240
7. Liang X R, Wei G J, Li X H, Liu Y. Rapid and precise measurement for $^{143}Nd/^{144}Nd$ isotopic ratio using a multi-collector inductively coupled plasma mass spectrometer. Rock and Mineral Analysis, 2002, 21(4): 247–251 (in Chinese)
8. Liang X R, Wei G J, Li X H, Liu Y. Precise measurement of $^{143}Nd/^{144}Nd$ and Sm/Nd ratios using a multi-collector inductively coupled plasma mass spectrometer (MC-ICPMS). Geochimica, 2003, 32(1): 91–96 (in Chinese)
9. Zhao M T, Zhou T, Wang J, Lu H, Fang X. Absolute measurements of Neodymium isotopic abundance and atomic weight by MC-ICPMS. International Journal of Mass Spectrometry, 2005, 245: 36–40
10. Xu P, Wu F Y, Xie L W, Yang Y H. Hf isotopic compositions of the standard zircons for u-pb dating. Chinese Science Bulletin, 2004, 49: 1403–1410 (in Chinese)
11. O'Nions R K., Hamilton P J, Evensen N M. Various in $^{143}Nd/^{144}Nd$ and $^{87}Sr/^{86}Sr$ ratio in oceanis basalts. Earth and Planetary Science Letters, 1997, 34: 13–22
12. Russell W A, Papanastassiou D A, Tombrello T A. Ca isotope fractionation on the earth and other solar system materials. Geochimca et Cosmochimca Acta, 1978, 42: 1075–1090
13. Pin C, Zalduegui J F S. Sequential separation of rare-earth elements, thorium and uranium by miniaturized extraction chromatography: application to isotopic analyses of silicate rocks. Analytica Chemica Acta, 1997, 339: 79–89
14. Wei G J, Liu Y, Tu X L, Liang X R, Li X H. Sepapation of Sr, Sm and Nd in mineral and rock samples using selective specific resins. Rock and Mineral Analysis, 2004, 23(1): 11–14 (in Chinese)