Bull. Natl. Mus. Nat. Sci., Ser. E, 36, pp. 1–5, December 22, 2013

Isotopic abundance measurements of Ca by using the new thermal ionization mass spectrometer installed at the National Museum of Nature and Science

Tatsunori YOKOYAMA[1]*, Keiji MISAWA[2,3] and Shigekazu YONEDA[1]

[1]Department of Science and Engineering, National Museum of Nature and Science, 4–1–1 Amakubo, Tsukuba, Ibaraki 305–0005, Japan
[2]National Institute of Polar Research, 10–3 Midoricho, Tachikawa, Tokyo 190–8518, Japan
[3]The Graduate University for Advanced Studies, 10–3 Midoricho, Tachikawa, Tokyo 190–8518, Japan
*e-mail: yokoyama.tatsunori@gmail.com

Abstract A new thermal ionization mass spectrometer (TIMS), Thermo Fisher Scientific TRITON plus, was installed at Department of Science and Engineering, Tsukuba research departments, National Museum of Nature and Science (NMNS) on October 2011. In order to obtain high precision Ca isotopic abundances of planetary materials, we have started to measure Ca isotopic ratio of the standard, NIST SRM915a, using the Faraday cups of the TRITON plus. The calcium isotopic data were acquired by a multidynamic mode using a Zoom Lens. In the measurement period between August 2012 and February 2013, an average value of $^{40}Ca/^{44}Ca$ of 15 analyses of NIST SRM 915a standard was $(^{40}Ca/^{44}Ca)_{SRM915a} = 47.1641 \pm 0.0040$ (2SD). The internal precisions of 192 ratio measurements were 22–48 ppm (2SE) and external precisions of 15 runs were 86 ppm (2SD).

Key words: thermal ionization, mass spectrometer, TRITON, Ca isotopic ratio

1. Introduction

The determination of precise ages of terrestrial and extraterrestrial rock formations using the decay of radioactive isotopes has been performed for several decades. Isotopic ratio measurements of calcium have been conducted mainly to investigate the isotopic anomaly of these rocks.

Calcium has six naturally occurring isotopes of ^{40}Ca, ^{42}Ca, ^{43}Ca, ^{44}Ca, ^{46}Ca, and ^{48}Ca with abundances of ^{40}Ca (96.941%), ^{42}Ca (0.647%), ^{43}Ca (0.135%), ^{44}Ca (2.086%), ^{46}Ca (0.004%) and ^{48}Ca (0.187%). ^{40}Ca is a β^- decay daughter of ^{40}K [$^{40}K = 0.01167\%$, $\lambda_K = 0.5543\ Ga^{-1}$, $\lambda_{\beta}{}^- / \lambda_K = 0.8952$, where λ_K and $\lambda_{\beta}{}^-$ are decay constants for total (β^-, β^+ and electron capture) ^{40}K disintegrations and β^- disintegration, respectively[1)]]. Marshall and DePaolo (1982, 1989)[2,3)] demonstrated that the ^{40}K–^{40}Ca decay system could be an important chronometer as well as a useful radiogenic tracer for studies of terrestrial rocks. However, K–Ca system has not been used as chronometer for meteorites, because meteorites contain several percent of calcium, whereas sub-percent potassium. Moreover, natural ^{40}Ca isotopic abundance is the highest among the Ca isotopes, and ^{40}K isotopic abundance is the lowest among the K isotopes. Recently, K-rich materials were found in extraterrestrial ordinary chondrites, differentiated achondrites and lunar samples. Therefore K–Ca system could be used to date such K-rich materials, but high precision Ca isotopic measurement is strongly required.

Thermo Fisher Scientific TRITON plus which is equipped with 9 Faraday cups and 1 Secondary Electron Multiplier (SEM) was installed at Department of Science and Engineering, Tsukuba research departments, National Museum of Nature and Science (NMNS)[4)]. The mass spectrometer makes possible the high precision

Ca isotopic measurements. Here we report high precision measurements of Ca standard (NIST SRM915a) that could be applied to measurements for planetary materials.

2. Analytical techniques

Zone-refined Re filaments were out-gassed at 4.5 A for 60 minutes. 2–3 μg (1 μl solution) Ca standards were loaded on the zone-refined Re filaments. Re–Re double filaments were used for the all analyses. Ca standards in HCl were evaporated with 2 μl 0.5 N phosphoric acid in order to facilitate adherence to the filaments. Samples were dried on the filaments at 0.5 A, and then evaporated at 1.5 A for about 2 minutes.

We ran the experiments on the TRITON plus using a multidynamic method. The mass spectrometer was operated in positive ionization mode with a 10-kV acceleration voltage and 10^{11} Ω resister for the Faraday cups. A stable ion-beam of 15 to 25 V on mass 40 is achieved at 1600℃ with ～3.7 to 3.9 A and ～1.4 to 1.5 A for ionization filament and evaporation filament, respectively. The analytical parameters are summarized in Table 1.

3. Cup configurations and Peak shapes

The multidynamic mode is made possible by Zoom Lens capability of the TRITON plus. The data acquisition parameters are shown in Table 2. Instrumental mass fractionation was corrected using conventional exponential law, with $^{42}Ca/^{44}Ca = 0.31221$[5] as the normalizing ratio. The ratio $^{42}Ca/^{44}Ca$ from Configuration 1 is used to correct for isotope fractionation of the $^{40}Ca/^{44}Ca$ and $^{48}Ca/^{44}Ca$ ratios within Configura-

Table 1. Experimental conditions used for Ca isotope analysis by TIMS TRITON plus

Property	Setting
Acceleration voltage	10 kV
Amplifier resistor	10^{11} Ω
Source vacuum	$6–8 \times 10^{-8}$ mbar (with liquid N_2 cold trap)
Analyzer vacuum	$4.5–4.8 \times 10^{-9}$ mbar
Cup gain calibration	Before measurements of each series
Baseline	Each block
	Integration time: 1.05 s
	Ion beam defocused
Peak centering	Each fourth block
Data collection	Blocks per run: 12 blocks
	Cycles per block: 16 cycles
	Integration time: 16.777 s for Faraday cup
	1.048 s for SEM
	Idle time: 7.00 s
Analyzing temperature	1600℃
Amplifier rotation (YES/NO)	YES (Left)

Table 2. Data acquisition parameter for Ca isotopes using TIMS TRITON plus at NMNS

Faraday Cups	L4	L3	L2	L1	C	H1	H2	H3	Zoom lenses	
									Focus	Dispersion
Configuration 1	^{39}K			^{40}Ca	^{41}K	^{42}Ca	^{43}Ca	^{44}Ca	−15	65
Configuration 2	^{43}Ca			^{44}Ca	(44.995)*	^{46}Ca	^{47}Ti	^{48}Ca	−0.9	10
Configuration 3	Ion Counter, IC1 (SEM) ^{47}Ti									

*dummy mass

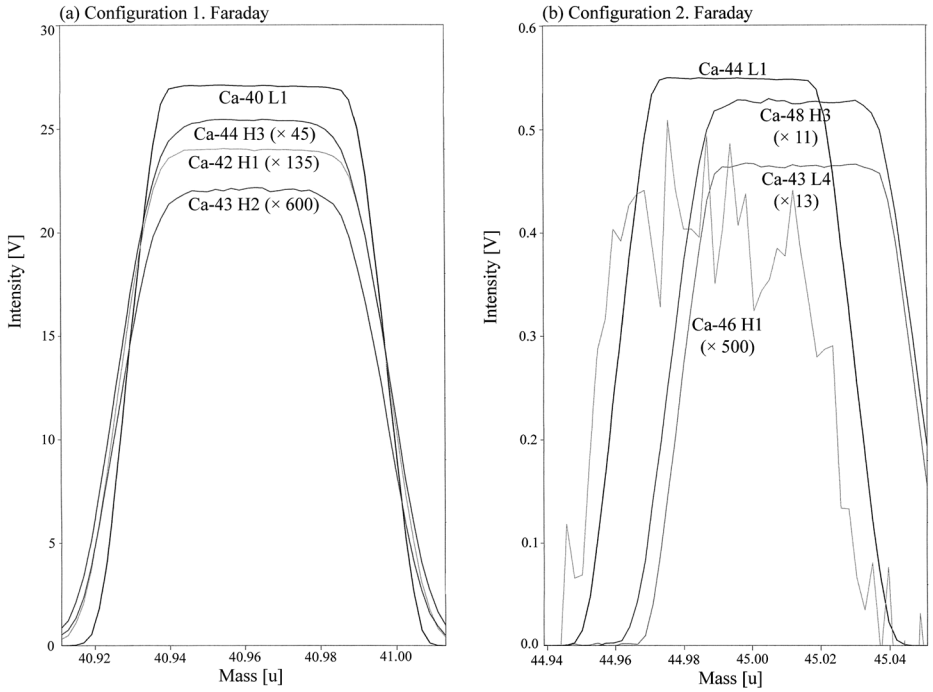

Fig. 1. Typical peak shapes of the Faraday collectors for (a) Configuration 1 and (b) Configuration 2. The values in the parentheses are the factors to clarify each peak shape.

tion 1 and 2, respectively. The isobaric interfering of ^{40}K with ^{40}Ca and ^{48}Ti with ^{48}Ca can be corrected by monitoring ^{39}K (and/or ^{41}K) and ^{47}Ti. We monitor ^{39}K and ^{47}Ti by Configuration 1 with Faraday cup and Configuration 3 with SEM, respectively.

Typical peak shapes of Ca ion of multidynamic measurements are shown in Fig. 1. The peak plateau flatness is excellent, but the overlap of each plateau center is not so good in Configuration 2. However, for the measurements of ^{40}Ca/^{44}Ca and ^{48}Ca/^{44}Ca, the influence of mismatched peaks is negligibly small.

4. Precision and Reproducibility

Results of 15 replicate runs of isotopic ratio measurements on the Ca standard (NIST SRM915a) are shown in Table 3 and Fig. 2. Results are represented with conventional ε^{40}Ca notation,

$$\varepsilon^{40}\mathrm{Ca} = \left\{ \left(\frac{^{40}\mathrm{Ca}}{^{44}\mathrm{Ca}} \right)_{sample} \Big/ \left(\frac{^{40}\mathrm{Ca}}{^{44}\mathrm{Ca}} \right)_{SRM915a} - 1 \right\} \times 10^4 ,$$

where

$$\left(\frac{^{40}\mathrm{Ca}}{^{44}\mathrm{Ca}} \right)_{SRM915a} = 47.1641 \pm 0.0040 (2\mathrm{SD})$$

is the average value of 15 analyses of SRM915a over the period between August 2012 and February 2013. The internal precision of 192 ratio measurements were 22–48 ppm (2SE) and external precisions of 15 runs were 86 ppm (2SD). Isobaric interference of ^{40}K which was always very small was corrected using ^{39}K and assumed natural ^{39}K/^{40}K ratio (^{39}K/^{40}K = 8075.0). Another possible isobaric interference of ^{48}Ti was also negligible with ^{47}Ti/^{48}(Ca + Ti) ratio was less than 1×10^{-5}. Our averaged ^{40}Ca/^{44}Ca value of SRM915a (^{40}Ca/^{44}Ca = 47.1641 ± 0.0040) is almost identical to that of Caro *et al.*

Table 3. Internal and external precision of Ca standard (NIST SRM915 a) at NMNS TIMS TRITON plus

Run	Date	$^{40}Ca/^{44}Ca$	Error (2SE)	% error (%)	$\varepsilon^{40}Ca$
1	Aug. 2012	47.1612	0.0019	0.0040	−0.61
2	Aug. 2012	47.1641	0.0017	0.0036	0.01
3	Aug. 2012	47.1661	0.0019	0.0040	0.44
4	Aug. 2012	47.1660	0.0016	0.0033	0.42
5	Aug. 2012	47.1647	0.0014	0.0029	0.13
6	Aug. 2012	47.1612	0.0023	0.0048	−0.62
7	Jan. 2013	47.1643	0.0010	0.0022	0.04
8	Feb. 2013	47.1634	0.0011	0.0023	−0.15
9	Feb. 2013	47.1665	0.0012	0.0026	0.51
10	Feb. 2013	47.1638	0.0011	0.0022	−0.07
11	Feb. 2013	47.1647	0.0011	0.0023	0.14
12	Feb. 2013	47.1680	0.0015	0.0031	0.83
13	Feb. 2013	47.1619	0.0011	0.0023	−0.46
14	Feb. 2013	47.1632	0.0013	0.0027	−0.20
15	Feb. 2013	47.1621	0.0013	0.0027	−0.43
Mean		47.1641	0.0040*	0.0086	

*Mean error: 2 × Standard Deviation (2SD)

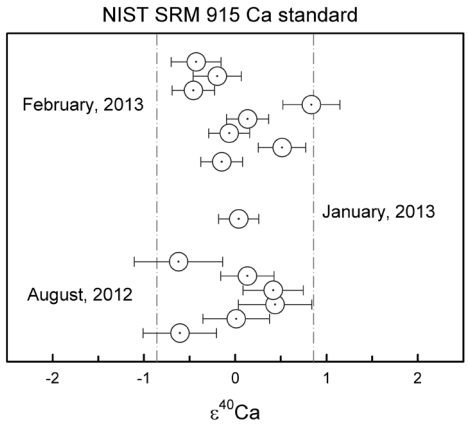

Fig. 2. Results of 15 replicate runs of isotopic ratio measurements on the Ca standard (NIST SRM 915a) using Faraday cups. $\varepsilon^{40}Ca = [(^{40}Ca/^{44}Ca)_{each\ value}/47.1641 - 1] \times 10^4$, where 47.1641 is an average value of $^{40}Ca/^{44}Ca$ ratio for SRM 915a standard (2SD = ± 0.0040, $n = 15$). Error bars are 2 sigma standard errors.

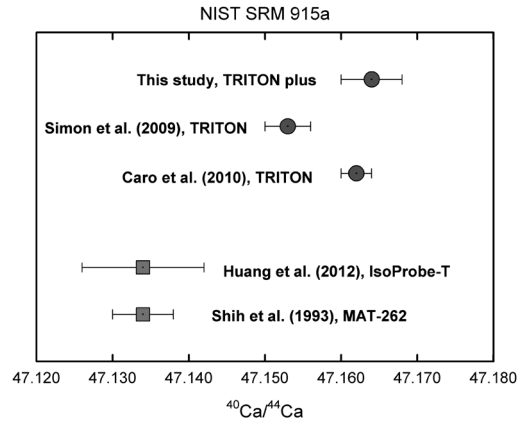

Fig. 3. Comparison of current NIST SRM 915a data obtained from TRITON (-plus) and other instruments. Error bars are 2 sigma standard deviations. Circle: Thermo TRITON (-plus), Square: GV IsoProbe-T or Finnigan MAT-262.

(2010)[6] ($^{40}Ca/^{44}Ca = 47.1622 \pm 0.0016$).

5. Possibility of instrumental bias

The summary of current SRM915a measurements data obtained by different laboratories using diverse TIMS, Shih *et al.* (1993)[7] (Finnigan MAT-262), Huang *et al.* (2012)[8] (GV IsoProbe-T), and Caro *et al.* (2010)[6], Simon *et al.* (2009)[9], and this study (Thermo TRITON (-plus)) are shown in Fig. 3. The $^{40}Ca/^{44}Ca$ isotopic ratios of SRM915a obtained by TRITON instruments are 0.02–0.03 higher than those obtained by IsoProbe-T and MAT-262. The TRI-

TON mass spectrometer is equipped with new generation amplifiers, which have 5 times wider dynamic ranges than those of previous instruments, and enable us to measure Ca ion beams of very high intensity. This may be the cause of the difference. For comparison between obtained data and reference data, we must pay attention to instrumental bias.

6. Conclusion

We obtained precise Ca isotopic data for SRM915a Ca standard. We have reported a Rb–Sr age of alkali-rich fragments in LL chondritic breccia[10]. We are trying to measure precise Ca isotopic composition and K–Ca isotopic systematical data of such K-rich planetary materials. These results imply that it is possible to obtain K–Ca ages of K-rich extraterrestrial materials.

Acknowledgements

We are thankful to Dr. Laurence E. Nyquist and Dr. Justin I. Simon of NASA Johnson Space Center, and Dr. Chi-Yu Shih and Mr. Michael J. Tappa of JETS/Jacobs Technology for their advices to the isotopic measurements of Ca using TRITON.

References

1) Steiger, R. H. and E. Jäger, 1977. Subcommission on geochronology: convention on the use of decay constants in geo- and cosmo-chronology. *Earth and Planet. Sci. Lett.*, 36: 359–362.
2) Marshall, B. D. and D. J. DePaolo, 1982. Precise age determinations and petrogenetic studies using the K-Ca method. *Geochim. Cosmochim. Acta,* 46: 2537–2545.
3) Marshall, B. D. and D. J. DePaolo, 1989. Calcium isotopes in igneous rocks and the origin of granite. *Geochim. Cosmochim. Acta*, 53: 917–922.
4) Yoneda, S., H. Hidaka, S. Machida, T. Yokoyama, K. Misawa, S. Sasaki and N. Kanazawa, 2012. Special features of the new thermal ionization mass spectrometer installed at the National Museum of Nature and Science, and their precision, reproducibility and long term stability on isotopic ratio measurements. *Bull. Natl. Mus. Nat. Sci., Ser. E*, 35: 1–6.
5) Russell, W. A., D. A. Papanastassiou and T. A. Tombrello, 1978. Ca isotope fractionation on the earth and other solar system materials. *Geochim. Cosmochim. Acta*, 42: 1075–1090.
6) Caro, G., D. A. Papanastassiou and G. J. Wasserburg, 2010. ^{40}K–^{40}Ca isotopic constraints on the oceanic calcium cycle. *Earth Planet. Sci. Lett.*, 296: 124–132.
7) Shih, C.-Y., L. E. Nyquist and H. Wiesmann, 1993. K–Ca chronology of lunar granites. *Geochim. Cosmochim. Acta*, 57: 4827–4841.
8) Huang, S., J. Farkaš, G. Yu, M. I. Petaev and S. B. Jacobsen, 2012. Calcium isotopic ratios and rare earth element abundances in refractory inclusions from the Allende CV3 chondrite. *Geochim. Cosmochim. Acta*, 77: 252–265.
9) Simon, J. I., D. J. DePaolo and F. Moynier, 2009. Calcium isotope composition of meteorites, Earth, and Mars. *Astrophys. J.*, 702: 707–715.
10) Yokoyama, T., K. Misawa, O. Okano, C.-Y. Shih, L. E. Nyquist, J. I. Simon, M. J. Tappa and S. Yoneda, 2013. Rb-Sr isotopic systematics of alkali-rich fragments in the Yamato-74442 LL-chondritic breccia. *Earth Planet. Sci. Lett.*, 366: 38–48.