Bull. Natn. Sci. Mus., Tokyo, Ser. E, 18, pp. 1–8, December 22, 1995

An Attempt of Isotopic Abundance Determination of Natural Radioactive Nuclides, ^{53}Mn and ^{230}Th, by Thermal Ionization Mass Spectrometry

By

Shigekazu YONEDA and Masako SHIMA

Department of Science and Engineering, National Science Museum,
3–23–1 Hyakunin-cho, Shinjuku-ku, Tokyo 169, Japan

and

Hiroshi HIDAKA and Mitsuru EBIHARA

Department of Chemistry, Tokyo Metropolitan University,
1–1 Minami-Osawa, Hachioji, Tokyo 192–03, Japan

Abstract

An attempt was made to determine the isotopic abundances of radioactive nuclides, ^{53}Mn and ^{230}Th, in the standard solutions extracted from a meteorite and a rock, respectively, using a thermal ionization mass spectrometer with an electro-static filter (ESF). The abundance sensitivity was checked by measuring the uranium isotopes and the baseline and was found to be 70 and 30 ppb (237/238) at the resolution power of 400 and 600, respectively. The Daly detector operated in the ion counting mode coupled with a Faraday cup enables the measurements of the extreme isotope ratios of the order of 10^{-6}. The measured ^{53}Mn/^{55}Mn and ^{230}Th/^{232}Th ratios are in good agreement with the literature values.

1. Introduction

A natural radioactive nuclide whose half life is less than $\sim 10^8$ yr is either a decay product of a nuclide with a half life of $\sim 10^9$ yr such as ^{232}Th, ^{235}U and ^{238}U, or a product of a nuclear reaction with the solar or cosmic rays, which is called a cosmogenic nuclide and is mainly found in meteorites. An example of the former is ^{230}Th (ionium; half life 7.54×10^4 yr), which is a daughter of ^{234}U (2.46×10^5 yr), and is produced in the decay series of ^{238}U (4.47×10^9 yr). The ionium/thorium ratio has been measured by α-ray counting and is used for dating deep sea sediment (GOLDBERG and KOIDE, 1962) and for estimation of the Th/U ratio of the magma sources of young volcanoes (KRISHNASWAMI *et al.*, 1984). An example of the latter is ^{53}Mn (3.7×10^6 yr), which is mainly produced by cosmic rays from iron with the reactions of ^{56}Fe(n, p3n), ^{54}Fe(n, 2n), or ^{56}Fe(p, α). It is found in meteoritic metal and gives us useful information regarding the

exposure ages and pre-atmospheric sizes of meteorites combining with other cosmogenic nuclides such as ^{26}Al (e.g. YABUKI and SHIMA, 1989; NISHIIZUMI, 1987). ^{53}Mn has been measured in many meteorites by X-ray counting (HONDA *et al.*, 1961), or by neutron activation analysis (MILLARD, 1965; IMAMURA *et al.*, 1969).

Recent development of mass spectrometry, especially an ion counting detector and improved ion optics, has enabled us direct and precise determination of a tiny isotope like these natural radioactive isotopes (PALACZ *et al.*, 1992). Here we report two such measurements: $^{53}Mn/^{55}Mn$ and $^{230}Th/^{232}Th$ which are of the order of 10^{-6}.

2. Experiments

2.1 Standard Solutions

The ^{53}Mn standard solution was originally extracted from a 500 g slice of the Grant iron meteorite at the University of California, La Jolla, with 9.1 mg Mn as a carrier (HONDA *et al.*, 1961). The extracted sample was then moved to the University of Tokyo, where it was recycled and calibrated by X-ray counting. The standard solution contains 5.24 ± 0.26 dpm ^{53}Mn/mg-Mn (HONDA and IMAMURA, 1971; IMAMURA, pers. comm., 1995), which corresponds to the $^{53}Mn/^{55}Mn$ ratio of $(1.34 \pm 0.07) \times 10^{-6}$.

The thorium standard solution (TML-1) was extracted from a Table Mountain latite at the University of California, Santa Cruz, and has a $^{230}Th/^{232}Th$ activity ratio of 1.070 determined by α-ray spectrometry (WILLIAMS as in PALACZ *et al.*, 1992). The activity ratio can be converted to the atomic ratio of $(5.76 \pm 0.05) \times 10^{-6}$.

2.2 Instrumentation

A VG Sector 54-30 thermal ionization mass spectrometer at the National Science Museum was used for this study. A schematic diagram of the mass spectrometer is shown in Fig. 1. It is equipped with a 54-cm-radius magnet followed by a 30-cm-radius electrostatic filter (ESF). Seven Faraday cup collectors are placed at the end of the magnet for simultaneous isotope measurements. One of them, called the axial Faraday cup, can be wound down by 25 mm and an ion beam pass through into the ESF. At the end of the ESF, a Daly detector system is placed. It is a combination of a Daly knob and a photomultiplier and is operated in the ion counting mode. Combining a Faraday detector and a Daly detector, extreme isotope ratios of the order of 10^{-6} can be measured.

2.3 Mass Spectrometry of Mn

A 1 μg of Mn was loaded on a rhenium ribbon single filament. Silica gel was placed on the sample in order to enhance the beam intensity of Mn and to reduce that of organic compounds. The $^{53}Mn/^{55}Mn$ ratios were determined via three

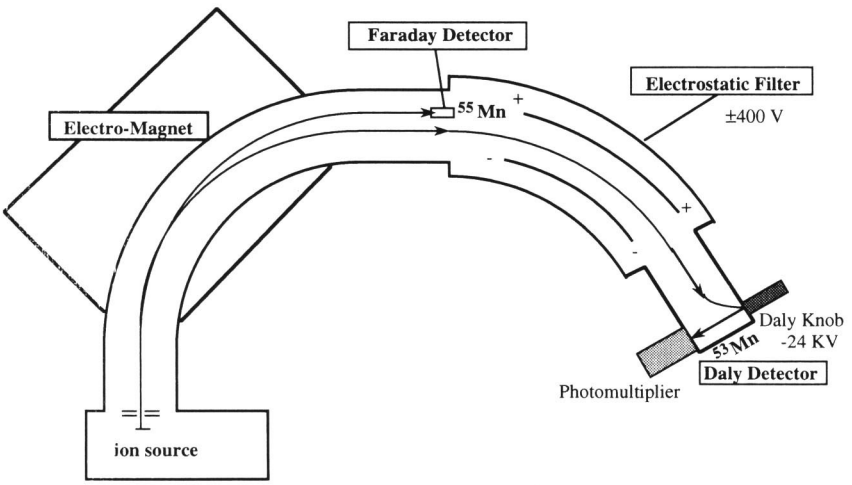

Fig. 1. A schematic diagram of a VG Sector 54-30 mass spectrometer. While ^{55}Mn is measured by the Faraday detector system, ^{53}Mn is measured by the Daly detector system through the electrostatic filter (ESF).

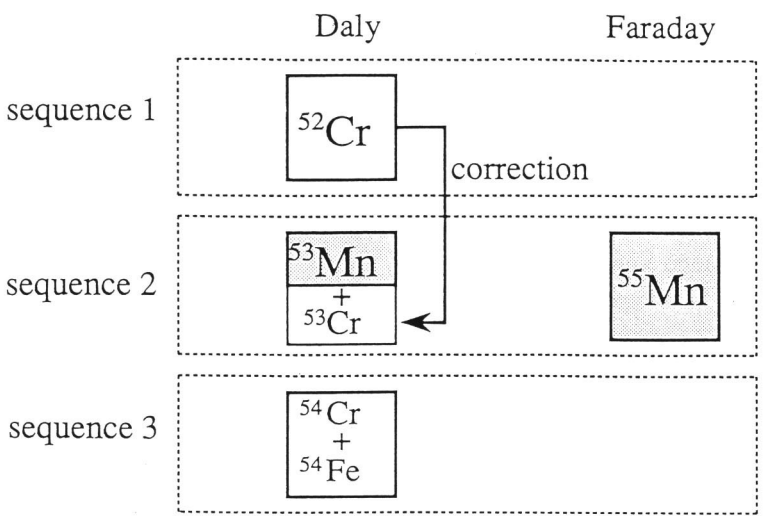

Fig. 2. The sequences for the $^{53}Mn/^{55}Mn$ measurements. The amount of the interference of ^{53}Cr on ^{53}Mn at the sequence 2 is calculated from the ^{52}Cr intensity at the sequence 1.

sequences shown in Fig. 2. Sequence 2 shows the static (simultaneous) measurement of ^{53}Mn and ^{55}Mn. The former was measured by the Daly detector, and the latter by the Faraday detector (Fig. 1). The sequences 1 and 3 were to determine the Cr interference on ^{53}Mn. The natural isotopic ratio of $^{53}Cr/^{52}Cr$ for the

correction was assumed since contribution of spallation-produced ^{53}Cr is reported to be negligible (SHIMA and HONDA, 1966). The filament currents used for the measurement were 2.1–2.6 A.

2.4 Mass Spectrometry of Th

A rhenium triple filament assemblage was used for the Th measurements. The side filaments were placed to face the center filament by tilting 45° in order to increase the ionization efficiency. It was pre-baked and any interference was checked by the mass spectrometer prior to sample loading. A 500 ng of Th was loaded on a side filament and the $^{230}Th/^{232}Th$ ratios were determined by the static mode where ^{230}Th was measured by the Daly detector and ^{232}Th by the Faraday detector simultaneously. The center filament currents were 4.2–4.7 A and the side filament currents were 2.1–2.7 A.

3. Results and Discussion

3.1 Faraday-Daly Gain Calibration

To calculate the isotopic ratios by the static mode, the gain difference between Faraday and Daly collectors must be known. This calibration was performed by measuring the same ion beam of $\sim 10^{-13}$ A by Faraday and Daly collectors alternately. The results using the ^{55}Mn beam are shown in Table 1. A mean value of 77.54 ± 0.16 was obtained. Using the ^{232}Th beam, also shown in Table 1, the Faraday-Daly gain factor was 95.30 ± 0.42 during the 8-hour measurements. Thus the variation of the gain factor at each mass was less than 0.5%. The difference between the gain factors of two measurements is due to the different settings of the machine parameters.

3.2 Abundance Sensitivity

A large ion beam may have a tail in the adjacent mass. This is a serious problem with the measurements of tiny isotopes. The abundance sensitivity is defined as the intensity of the tail, usually the baseline of the adjacent mass, relative to the ion beam intensity. The ^{238}U and ^{234}U ion beams were used to

Table 1. Faraday/Daly gain factors on VG Sector 54-30.

Block*	Factor by ^{55}Mn	Factor by ^{232}Th
1	77.36 ± 0.06	95.58 ± 0.11
2	77.69 ± 0.05	95.44 ± 0.06
3	77.44 ± 0.02	95.90 ± 0.04
4	77.66 ± 0.02	94.91 ± 0.04
5		94.81 ± 0.04
6		95.18 ± 0.03
Average	77.54 ± 0.16	95.30 ± 0.42

* Each block consists of 10 measurements. Errors are 1σ.

determine the abundance sensitivity. They are in radioactive equilibrium in the natural samples with $^{234}U/^{238}U = \sim 55$ ppm. Combining this ratio with the measured intensities at masses 234 and 237, the abundance sensitivity at mass 237 relative to ^{238}U can be obtained.

At the vacuum of 4×10^{-8} mbar in the ion source chamber, it was 69.5 ± 3.5 ppb at the resolution power 400 with the 1.0 mm collector slit. At the resolution power 600 with the 0.7 mm collector slit, it was 29.5 ± 2.2 ppb. This is by far superior to that of VG 54 without the ESF (2000 ppb: PALACZ *et al.*, 1992).

3.3 $^{53}Mn/^{55}Mn$ Isotopic Ratio

An example of the ^{53}Mn and ^{55}Mn ion beams is illustrated in Fig. 3. The ion beam intensity of ^{55}Mn measured by the Faraday detector was $\sim 5 \times 10^{-12}$ A, and that of ^{53}Mn measured by the Daly detector was $\sim 0.65 \times 10^{-17}$ A, giving an isotopic ratio of $\sim 1.3 \times 10^{-6}$. The correction of the ^{53}Cr interference on ^{53}Mn calculated from the intensity of ^{52}Cr was small (10–20% of the total intensity). The results of 4 measurement runs, each of which is the average of ~50 ratios, are plotted as a function of the filament current in Fig. 4. The mass fractionation effect with the filament current, hence the temperature, are clearly seen. The ratios are, however, in good agreement with the X-ray counting data except for the lowest temperature result.

3.4 $^{230}Th/^{232}Th$ Isotopic Ratio

The measured ^{232}Th beam intensities were $2\text{–}5 \times 10^{-12}$ A. The excellent reproducibility of 6 independent analyses (100 ratios each) can be seen in Fig. 5.

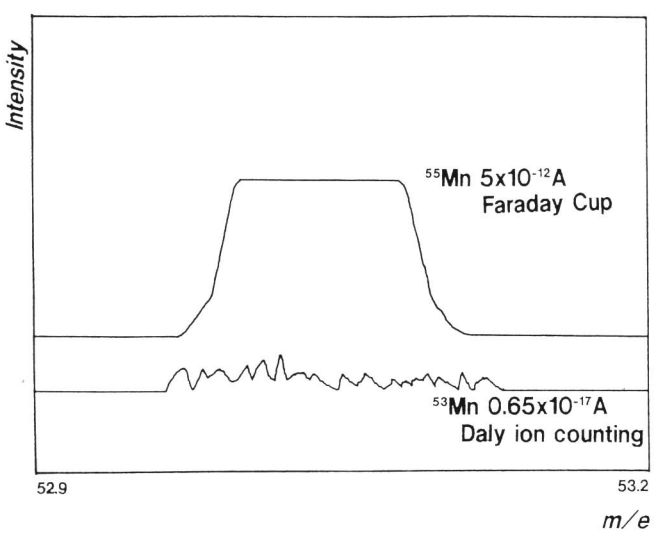

Fig. 3. An example of the mass-scan in the range 52.9–53.2 at the Daly detector position. At the Faraday detector position, it corresponds to 54.9–55.2. The full range of the intensity are 10^{-11} A and 10^{-16} A for ^{55}Mn and ^{53}Mn, respectively.

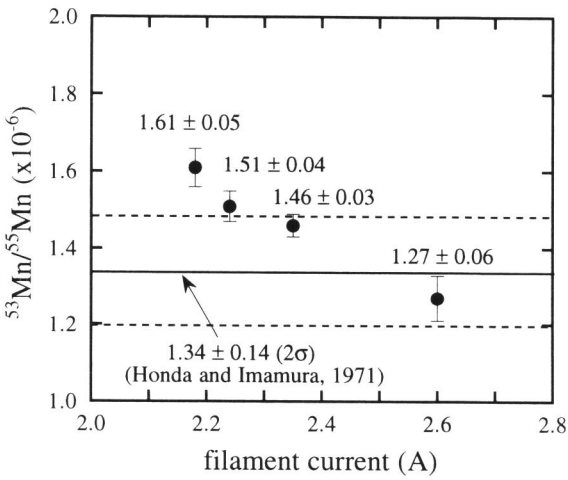

Fig. 4. The results of the $^{53}Mn/^{55}Mn$ ratios plotted against the filament currents. Error bars represent the standard errors (2σ) of ~50 ratios. Data by X-ray counting (HONDA and IMAMURA, 1971) are also shown.

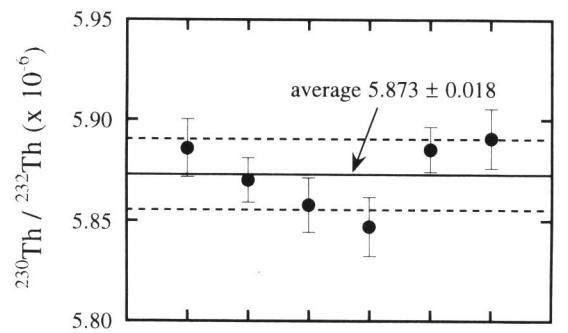

Fig. 5. The results of 6 repetitive measurements of $^{230}Th/^{232}Th$ ratios. Each measurement is an average of 100 ratios.

The overall average is listed in Table 2 with the literature values. The data by mass spectrometry including those in this study are in good agreement with one another while the data by α-ray spectrometry are slightly smaller.

3.5 Applications and Limitations

The Faraday detector system is capable to measure a beam intensity up to 10^{-10} A. Thus, if the intensity of the larger peak is strong enough, an isotopic ratio of 5×10^{-8} can be measured. The effect of the beam tail in the adjacent mass (i.e. the abundance sensitivity) is also the order of 10^{-8}, but, when the isotopes measured are 2 mass number apart, it is negligible. The beam intensity is, however, limited by the amount of the sample loaded on the filament and the ionization efficiency. In the future work, we will examine the effect of the

Table 2. Comparison of $^{230}Th/^{232}Th$ data obtained from the measurement of the thorium standard TML-1.*

Laboratory	Instrument	$^{230}Th/^{232}Th$ ($\times 10^{-6}$)	Reference
UCSC	Alpha Spec	5.76±0.05	WILIAMS, as in PALACZ *et al.* (1992)
Los Alamos	Nier Double Focusing	5.84±0.03	GOLDSTEIN *et al.* (1989)
Open Univ.	Finnigan MAT261 (without ESF)	5.80±0.06	MCDERMOTT *et al.* (1993)
VG Isotech	VG 54-30 (with ESF)	5.88±0.03	PALACZ *et al.* (1992)
Natl. Sci. Mus.	**VG 54-30 (with ESF)**	**5.87±0.02**	**this study**

* Extracted from Table Mountain Latite (TML) by UCSC.

activators, such as noble metal powders and boric acid, in order to increase the efficiency.

The $^{53}Mn/^{55}Mn$ ratios in the iron meteorites are $\sim 3 \times 10^{-4}$ with the Mn concentrations of ~0.3 ppm (HONDA and IMAMURA, 1971). These ratios can be measured easily if the sufficient amounts of samples are obtained (~3 g of iron meteorites is required to recover 1 μg of Mn.) It is, however, necessary to establish a suitable measurement condition to avoid the large mass fractionation observed in this study. On the other hand, those in the stony meteorites are expected to be the order of 10^{-8} with the Mn contents of ~2000 ppm. While only 0.5 mg of meteorites is required for the measurement with 1 μg Mn, its extremely low isotopic abundance places the great demands on the performance of the mass spectrometer. Longer integration time and larger Daly detector gains may be helpful for these measurements.

Acknowledgments

We are indebted to VG Isotech technicians, Drs. C. WEBB, C. MAYERS and Z. A. PALACZ, for assistance of mass spectrometry and providing the Th standard solution. We are thankful to Dr. M. IMAMURA of the Institute for Nuclear Studies, the University of Tokyo, for providing us the ^{53}Mn standard solution and helpful comments. This work was supported in part by a Grant-in-Aid for Scientific Research of Ministry of Education, Science and Culture, Japan (No. 05217214 to M.S., No. 07640659 to H.H. and No. 05453012 to M.E.).

References

GOLDBERG, E. D. and M. KOIDE, 1962. Geochronological studies of deep sea sediments by ionium/thorium method. *Geochim. Cosmochim. Acta*, 26: 417–450.

GOLDSTEIN, S. J., M. T. MURRELL and D. R. JANECKEY, 1989. Th and U isotopic systematics of

basalts from Juan de Fuca and Gorda Ridges by mass spectrometry. *Earth Planet. Sci. Lett.*, 96: 134–146.

HONDA, M. and M. IMAMURA, 1971. Half-life of Mn^{53}. *Physical Review*, 4: 1182–1188.

HONDA, M., J. P. SHEDLOVSKY and J. R. ARNOLD, 1961. Radioactive species produced by cosmic rays in iron meteorites. *Geochim. Cosmochim. Acta*, 22: 133–154.

IMAMURA, M., H. MATSUDA, K. HORIE and M. HONDA, 1969. Application of neutron activation method for ^{53}Mn in meteoritic iron. *Earth Planet. Sci. Lett.*, 6: 165–172.

KRISHNASWAMI, S., K. K. TUREKIAN and J. T. BENNETT, 1984. The behavior of ^{232}Th and the ^{238}U decay chain nuclides during magma formation and volcanism. *Geochim. Cosmochim. Acta*, 48: 505–511.

MCDERMOTT, F., T. R. ELLIOTT, P. van CALSTEREN and C. J. HAWKESWORTH, 1993. Measurement of $^{230}Th/^{232}Th$ ratios in young volcanic rocks by single-sector thermal ionisation mass spectrometry. *Chem. Geol.*, 103: 283–292.

MILLARD, H. T. Jr., 1965. Thermal neutron activation: Measurement of cross section for manganese-53. *Science*, 147: 503–504.

NISHIIZUMI, K., 1987. ^{53}Mn, ^{26}Al, ^{10}Be and ^{36}Cl in meteorites: Data compilation. *Nucl. Tracks Radiat. Meas.*, 13: 209–273.

PALACZ, Z. A., P. A. FREEDMAN and A. J. WALDER, 1992. Thorium isotope ratio measurements at high abundance sensitivity using a VG 54-30, an energy-filtered thermal ionization mass spectrometer. *Chem. Geol.*, 101: 157–165.

SHIMA, M. and M. HONDA, 1966. Distribution of spallation produced chromium between alloys in iron meteorites. *Earth Planet. Sci. Lett.*, 1: 65–74.

YABUKI, S. and M. SHIMA, 1989. Cosmogenic ^{26}Al and ^{53}Mn in Japanese chondrites. *Bull. Natn. Sci. Mus., Ser. E*, 12: 1–14.