

Precise tellurium isotope analysis by negative thermal ionization mass spectrometry (N-TIMS)

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We present a new method for precise isotope analysis of Te by thermal ionization mass spectrometry in negative ion mode (N-TIMS) along with an improved technique for chemical separation of Te from geochemical samples. In the chemical separation, Te was purified by a three-step column chemistry method employing an anion exchange resin and an extraction chromatographic resin, yielding 98% recovery. To achieve strong Te^- beam intensity in N-TIMS, we evaluated the optimum analytical conditions with respect to the filament material, ionization activator, and filament heating protocol. The reproducibilities of Te isotope ratios obtained by static multicollection using Faraday cups were 0.9%, 0.04%, 0.06%, 0.01%, 0.005%, and 0.008% for $^{120}\text{Te}/^{128}\text{Te}$, $^{122}\text{Te}/^{128}\text{Te}$, $^{123}\text{Te}/^{128}\text{Te}$, $^{125}\text{Te}/^{128}\text{Te}$, $^{126}\text{Te}/^{128}\text{Te}$, and $^{130}\text{Te}/^{128}\text{Te}$, respectively. This result is comparable to those of previous MC-ICP-MS studies. The reproducibilities of Te isotopes obtained by SEM jumping measurements were approximately ten times worse than those obtained by Faraday cup runs, excluding the $^{120}\text{Te}/^{128}\text{Te}$ ratio for which the reproducibility was comparable to that obtained by Faraday cup runs due to the extremely low abundance of ^{120}Te . To further improve the analytical precision, the $^{126}\text{Te}/^{128}\text{Te}$ ratio was determined by multidynamic collection for the study of ^{126}Sn – ^{126}Te chronology. The 2s of the $^{126}\text{Te}/^{128}\text{Te}$ ratio of the multidynamic collection was 1.6 times better than that obtained by static measurements. Finally, the accuracy of our method was confirmed by the analysis of two carbonaceous chondrites and one terrestrial standard rock, which was consistent with previously reported values.

1. Introduction

Precise and accurate analysis of stable isotope compositions for heavy elements in a variety of natural samples is acquiring more importance in geosciences. In nature, stable isotope fractionation follows the mass-dependent fractionation (MDF) law,¹ whereas mass-independent fractionation (MIF) is observed in some limited cases. MDF occurs either in chemical equilibrium due to the difference in equilibrium constants for different isotopes or in kinetic processes such as evaporation and condensation. The degree of MDF is significant for light elements such as H, C, N, and O, but is relatively small for heavy elements because of the small relative mass differences between their isotopes. On the other hand, MIF is observed in samples that experience specific natural processes such as photochemical reactions in the stratosphere and troposphere.² For meteorites, incorporation of isotopically anomalous materials that were synthesized in various stellar environments can further cause isotopic shifts that do not follow the MDF law. The MIF effect is expected to be smaller for heavy elements than light elements. For example, the magnitude of $\Delta^{17}\text{O}$ variation in meteorites can be on the order of several percents,³ whereas

nucleosynthetic Mo isotope anomalies in meteorites are at a level of less than a few per mil.⁴ However, recent progress in mass spectrometry techniques has enabled detection of extremely small differences in isotope ratios at the ppm level.^{5,6} To precisely and accurately determine such minuscule differences in isotope ratios, it is essential to develop not only instrumental techniques but also sample preparation methods including sample digestion and chemical separation. For example, high purity chemical separation of elements of interest from unwanted elements that have potential isobaric interference is specifically important for mass spectrometry.

Tellurium is an intriguing element in geosciences. It has eight naturally occurring isotopes: 120, 122, 123, 124, 125, 126, 128, and 130. Cosmochemically, these isotopes are produced during stellar nucleosynthesis by the p-process (^{120}Te), the s-process (^{122}Te , ^{123}Te , and ^{124}Te), and the r-process (^{128}Te and ^{130}Te). Both the s- and r-processes produce ^{125}Te and ^{126}Te . Therefore, tellurium is suitable for investigating excesses (or absence) of specific isotopes that result from the inclusion of nucleosynthetic materials. Furthermore, the tellurium isotope compositions are affected by the short-lived nuclide of ^{126}Sn that decays to ^{126}Te with a half-life of 234.5 kyr.⁷ This decay system could be a clue for understanding processes that occurred in the early solar system; however, no ^{126}Te excess in meteorites due to high Sn/Te ratios has been reported so far.⁸ In

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contrast, anomalous Te isotope compositions (^{128}Te and ^{130}Te) have been reported for presolar nanodiamonds extracted from a carbonaceous chondrite.^{9,10}

Historically, Te isotope measurements have been performed by thermal ionization mass spectrometry (TIMS) in positive ion mode (Te^+ ; P-TIMS) using a Re filament and a silica gel activator.^{11–13} In contrast, Wachsmann and Heumann (1992) measured Te isotope compositions using TIMS in negative ion mode (N-TIMS) with a Re double filament and $\text{Ba}(\text{OH})_2$ activator.¹⁴ More recently, Te isotopes have been analyzed using multi-collector inductively coupled plasma mass spectrometry (MC-ICP-MS).^{15,16} Fehr *et al.* (2004) achieved 44 ppm of analytical uncertainty while measuring $^{126}\text{Te}/^{128}\text{Te}$ ratios using MC-ICP-MS. This result was approximately six times smaller than those of previous N-TIMS measurements.¹⁶ However, precise Te isotope analysis using state-of-the-art TIMS has not been examined.

In this study, we have developed a method for precise Te isotope analysis by N-TIMS using a next generation TIMS instrument (TRITON-*plus*). Taking particular interest in the analytical precision of $^{126}\text{Te}/^{128}\text{Te}$, a key isotope ratio for the application of ^{126}Sn – ^{126}Te systematics, we examined the multidynamic collection technique in N-TIMS measurements. In addition to the mass spectrometry technique, we developed a new chemical separation procedure using an anion exchange resin and an extraction chromatographic resin. Finally, we report precise Te isotopic compositions of some terrestrial and extraterrestrial materials.

2. Experimental

2.1. Reagents

EL-grade HCl and HNO_3 (Mitsubishi Chemical, Japan), and AAS-grade HF were distilled once using a two-bottle Teflon distillation system. Tamapure AA100-grade HClO_4 (Tama Chemical, Japan) was employed without distillation. Pure water (specific resistance = 18.2 $\text{M}\Omega\text{ cm}$) was prepared using a water purifying system (Milli-Q Integral 5, Merck Millipore).

A $\text{Ba}(\text{OH})_2$ solution containing NaOH was prepared as the TIMS ionization activator. Approximately 10 g of $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ (Merck, Germany) was mixed with 20 mL of H_2O and thoroughly agitated, and then the supernatant was removed. This washing procedure was repeated several times. The washed $\text{Ba}(\text{OH})_2$ was mixed with 40 mL of a 0.1 M NaOH solution and completely dissolved in a closed bottle by heating at 80 °C for a few hours. The solution was cooled down to room temperature to ensure recrystallization of $\text{Ba}(\text{OH})_2$, and the supernatant was used as the ionization activator.

2.2. Samples

To evaluate the performance of chemical separation and isotope analysis by TIMS, a terrestrial rock (JB-3) and two carbonaceous chondrites (Murchison and Allende) were examined. JB-3 is a basaltic rock prepared by the Geological Survey of Japan as a geochemical reference sample. The Murchison and Allende

meteorites are classified as CM2 and CV3, respectively. Carbonaceous chondrites are early solar system materials that have not been modified by melting or differentiation of their parent bodies. These powdered rock samples were digested in a pressure digestion system, DAB-2 (Berghof, Germany), using HF and HNO_3 at 220 °C for over 40 h. The digested samples were evaporated to dryness once and dried down three times with a few drops of 12 M HCl. Next, the samples were dissolved in 2 M HCl for the subsequent chemical separation procedure (Section 2.3.1).

For isotope analysis by TIMS, we used a Te standard solution (Kanto Chemical, Japan) as our in-house standard. To convert the chemical form, the standard solution (in HNO_3 form) was evaporated to dryness and dissolved in 1 M HCl.

2.3. Chemical separation

2.3.1 Column chemistry. Tellurium was separated using a three-step column chemistry method as indicated in Table 1, which was a modification of the technique used by Fehr *et al.* (2004).¹⁶ All chemical procedures were performed in a class 100 clean room at the Tokyo Institute of Technology. In the first separation step, 2 mL of AG1-X8 (200–400 mesh, BioRad) was charged in a polypropylene column (resin bed: $\phi = 8$ mm, $h = 39$ mm). A 15 mL solution of 2 M HCl containing the dissolved sample was loaded on the resin. Then, 10 mL of 2 M HCl, 4 mL of 12 M HCl, and 4 mL of 5 M HF were successively added to the column in which a majority of the elements were eluted. Finally, Te along with Sn was recovered using 10 mL of 1 M HNO_3 .

A 0.2 mL TRU-Spec resin (Eichrom, USA) was charged in a second polypropylene column (resin bed: $\phi = 4$ mm, $h = 16$ mm), and a 0.1 mL Amberchrom CG-71C was charged in

Table 1 Chemical separation procedure of Te

Eluent	Volume [mL]		
First column: 2 mL BioRad AG1-X8 resin, 200–400 mesh			
1 M HNO_3	10	Resin cleaning	40
H_2O	10	Resin cleaning	
2 M HCl	10	Resin conditioning	
2 M HCl (sample load)	15	Matrix	
2 M HCl	15	Matrix	
12 M HCl	4	Matrix	45
5 M HF	15	Matrix	
1 M HNO_3	10	Sn, Te	
Second column: 0.2 mL Eichrom TRU-Spec resin and 0.1 mL Amberchrom CG-71C			
0.5 M HCl	10	Resin cleaning & conditioning	50
0.5 M HCl (sample load)	1	Te	
0.5 M HCl	5	Te	
Third column: 0.01 mL BioRad AG1-X8 resin, 200–400 mesh			
1 M HNO_3	50	Resin cleaning	55
H_2O	200	Resin cleaning	
12 M HCl	100	Resin conditioning	
12 M HCl (sample load)	100	Matrix	
5 M HF	50	Matrix	
1 M HNO_3	100	Te	

another column (resin bed: $\phi = 4$ mm, $h = 8$ mm). The latter column was placed under the former column in tandem style to transfer the eluent from the TRU-Spec. The Te fraction obtained from the first column was dried and conditioned with 1 mL of 0.5 M HCl. This solution was loaded on the resin, and 5 mL of 0.5 M HCl was added to the column. Te was recovered using 0.5 M HCl during this step, whereas Sn was adsorbed onto the resin and not eluted.

The Te fraction from the second step was dried and conditioned with 0.1 mL of 12 M HCl, which was loaded on the third column. The third column chemistry was performed using 0.01 mL of AG1-X8 resin charged in a polypropylene column (resin bed: $\phi = 1.4$ mm, $h = 6.5$ mm). Next, 0.1 mL of 12 M HCl and 0.05 mL of 5 M HF were successively added to the column to further remove organic matter derived from the resin in the previous step. Then, Te was recovered using 0.1 mL of 1 M HNO₃.

The final fraction was dried and dissolved in a few drops of concentrated HNO₃ + HClO₄. This fraction was evaporated to dryness to remove the remaining organic matter. The purified Te fraction was redissolved in 1 M HCl and subjected to the subsequent Te isotope analyses.

2.3.2 Determination of elution curves. To determine the elution curves of multiple elements in each column chemistry step, we prepared a JB-3 solution doped with Te (1 μ g of Te per 200 mg of JB-3). The fractions from individual columns were dried and dissolved in 0.5 M HNO₃ to determine the major and trace element concentrations by the calibration curve method using a quadrupole-type ICP-MS (X series II, Thermo Fisher Scientific) installed at the Tokyo Institute of Technology.

2.4. Thermal ionization mass spectrometry

2.4.1 Loading and heating procedures. All Te isotope measurements were performed by N-TIMS (TRITON *plus* at the Tokyo Institute of Technology, Thermo Fisher Scientific). The instrument is equipped with nine Faraday cups and 10¹¹ Ω amplifiers. A secondary electron multiplier (SEM) is connected behind the center Faraday cup.

We tested three filament materials: W (thickness = 0.0254 mm, width = 0.762 mm; Nilaco, Japan), Re (thickness = 0.0254 mm, width = 0.762 mm; Nilaco, Japan), and zone-refined Re (thickness = 0.0305 mm, width = 0.750 mm; H. Cross, USA). Before sample loading, the W and Re filaments were degassed in a vacuum for 30 min at 5.4 A and 4.5 A, respectively. The sample was dissolved in 1 μ L of 1 M HCl and loaded on the center of the filament, which was covered in the saturated Ba(OH)₂ solution containing NaOH. In addition, we tested two activators: silicic acid and a La–Gd mixed solution. We observed that the Te[−] beam intensity was dependent on the filament material as well as on the amount of Ba(OH)₂ covering the sample. An optimum condition for ionizing Te was obtained when the sample was loaded on the zone-refined single Re filament (H. Cross) along with 250 μ g of Ba(OH)₂, irrespective of the amount of Te (see Section 3.2.1).

The filament was heated to 0.5 A at a rate of 0.5 A min^{−1}. Then, the rate was decreased to 0.15 A min^{−1} until the current reached 0.9 A. Subsequently, the heating rate was fixed at 0.05 A min^{−1}, and the current was increased in a stepwise manner. At 740 °C

Table 2 A configuration for Faraday cup measurement

	L4	L3	L2	L1	Center	H1	H2	H3	Integration
Line 1	¹²² Te	¹²³ Te	¹²⁴ Te	¹²⁵ Te	¹²⁶ Te	¹²⁷ I	¹²⁸ Te	¹³⁰ Te	16 s
Line 2	¹²⁰ Te	¹²¹ Sb	¹²² Te	¹²³ Te	¹²⁴ Te	¹²⁵ Te	¹²⁶ Te	¹²⁸ Te	16 s

(1.10–1.25 A), the current was maintained for 30 min for out-gassing. Then, the filament was heated to 810–860 °C until the Te[−] ion beam intensity stabilized. At this temperature, 200 ng of Te produced a ¹²⁶Te[−] ion beam intensity of approximately 0.2–0.8 V (2–8 $\times 10^{-12}$ A). The ion beam intensities decayed to approximately one third of the initial value during the analytical session.

2.4.2 Measurement of Te isotope ratios. Isotope ratios were acquired using either Faraday cups (FCs) or an SEM connected behind the center Faraday cup. Our instrument has nine Faraday cup collectors; however, not all eight Te isotopes can be simultaneously collected because of limitations in collector geometry. Therefore, we used the zoom optics option to collect all Te isotopes, and the isotope measurements were performed by a two-line analytical setting described in Table 2. This configuration was chosen to enable the measurement of ¹²⁶Te/¹²⁸Te ratios in multidynamic collection, because precise and accurate analysis of ¹²⁶Te/¹²⁸Te ratios is important for ¹²⁶Sn–¹²⁶Te chronology studies. For this purpose, the center Faraday cup and H2 Faraday cup were set to obtain the ¹²⁶Te/¹²⁸Te ratio (line 1) and the ¹²⁴Te/¹²⁶Te ratio (line 2), respectively. The data were obtained by taking the mean of 160 cycles with 2 s (2 standard deviations) rejection in each block (8 block measurements, 20 scans per block, 16 s integration per scan). The baseline measurement was performed at the start of every block. Peak centering and ion beam focusing were conducted in each of the three blocks of measurement. To minimize the uncertainty in amplifier gain calibration, the amplifier rotation system of the TRITON was applied for all analyses.

When the ¹²⁶Te[−] beam intensity was lower than 0.03 V, all isotopes were measured in a jumping mode by SEM. In the SEM measurements, the filament temperature was adjusted so as not to exceed 300 000 cps of the ¹³⁰Te[−] ion beam intensity to protect the collector and to minimize the propagation of uncertainties in the SEM dead time. One measurement session consists of 5 runs of 51 cycles. The data were obtained by averaging 5-run measurements.

All the Te isotope ratios obtained in both the Faraday cup and SEM measurements were corrected for mass fractionation by normalizing ¹²⁴Te/¹²⁸Te to be 0.14853 (ref. 15) using the exponential law to directly compare our data with those of previous studies that used MC-ICP-MS.^{15,16} The magnitude of the corrections for mass fractionation varied from sample to sample, but it was typically 1‰ per amu from the beginning of the measurement to the end of the measurement.

3. Results and discussion

3.1. Chemical separation of Te

Fig. 1 shows the elution curve of the first column chemistry step using Te-doped JB-3 as the loading solution. Major elements in

the rock sample, such as Mg, Ca, Fe, and Al, do not form anion complexes with HCl, and they were not adsorbed onto the resin under the loading condition (2 M HCl). However, Zn was adsorbed slightly onto the resins in 2 M HCl, and a small proportion of Zn was mixed into the Te fraction when the previous method¹⁶ was applied. To facilitate Zn removal, we increased the amount of 2 M HCl from 10 mL to 15 mL in the washing step after sample loading. Likewise, the amount of 5 M HF was increased from 4 mL to 15 mL. Consequently, the amount of Zn remaining before Te collection was significantly reduced (Fig. 1), and the beam intensity obtained from the final Te fraction was approximately ten percent larger than the Te fraction prepared by the previous method. Sb, which has isobaric interference with ¹²³Te (¹²³Sb), was separated from Te in the loading and subsequent washing steps using 2 M HCl and 12 M HCl. The resulting Sb/Te ratio in the Te fraction was less than 0.3%. The recovery yield of Te in the first column was 98%. In the cases of carbonaceous chondrite samples, the first column step was repeated twice because we observed that less than 0.1% of matrix elements remained in the Te fraction after this repetition.

In contrast, Sn, another isobaric element, could not be separated from Te in the first column. Sn remaining in the Te fraction after the first column was separated in the second column using the TRU resin. In 0.5 M HCl, Sn was adsorbed onto the resin, while Te was not adsorbed and was eluted with HCl. After the second column, the Te fraction was passed through the third column. The third column was used for reducing the amount of organic matter remaining from the TRU

resin, because we observed that without the third column treatment, Te ion beam intensities in the N-TIMS measurement decreased by 20%. The yield of the three-step column chemistry was $98 \pm 6\%$.

3.2. TIMS analytical conditions

In previous TIMS studies, Te isotope compositions were measured in positive ionization mode using a single Re filament with silica gel as an activator.^{11–13} The beam intensity obtained by P-TIMS using 250 ng of Te was 2×10^{-13} A (¹³⁰Te⁺), which decreased to 2×10^{-14} A over the analytical period.¹⁷ The analytical uncertainty for the P-TIMS measurement was approximately 300 ppm for ¹²⁶Te/¹²⁸Te. In contrast, Wachsman and Heumann (1992) measured Te isotope compositions by N-TIMS with a Re double filament and Ba(OH)₂ activator.¹⁴ Their N-TIMS measurement was performed with an ion beam intensity of approximately 10^{-12} A (¹³⁰Te⁻) using 1 μg of Te and analytical uncertainties of approximately 3‰ for ¹²⁶Te/¹²⁸Te.

In TIMS analysis, the ion beam intensity varies with the amount of target element loaded onto the filament. The other factors that control the ion beam intensity are the filament material, filament temperature and amount of activator. To achieve better performance compared to the previous TIMS measurements described above, we have evaluated the analytical conditions as follows.

3.2.1 Filament material and amount of activator. First, we tested three different filament materials. When 200 ng of Te was loaded onto the filament with the Ba(OH)₂ activator, the maximum beam intensities of ¹²⁶Te⁻ were 70, 300, and 600 mV for the W, Re (Nilaco), and Re (H. Cross) filaments, respectively. The correlation of beam intensity with filament type did not change significantly when the amount of Te was changed. Therefore, we employed the zone-refined Re (H. Cross) filament in the following experiments.

We tested three ionization activators: Ba(OH)₂, silicic acid, and a La–Gd mixed solution. The combination of the Re filament (H. Cross) and the Ba(OH)₂ activator resulted in a sufficient beam intensity ($\sim 10^{-12}$ A for ¹²⁶Te⁻) when 200 ng of Te was loaded, whereas the Te⁻ beam intensity was less than 10^{-13} A when the other activators were used. The other combinations (e.g., W filament with La–Gd mixed solution) did not outperform the combination of Re (H. Cross) and Ba(OH)₂. Therefore, we decided to use Ba(OH)₂ as the activator for N-TIMS. To determine the optimum amount of Ba(OH)₂, we measured the Te⁻ beam intensity of our in-house standard by varying the amount of Te (200–500 ng) and activator (5–2500 μg). The procedure of filament heating is described in Section 2.4.1. The maximum beam intensity for an individual amount of Ba(OH)₂ was measured at 870 °C. As shown in Fig. 2, the maximum Te⁻ beam intensity in a single measurement was obtained when 250 μg of Ba(OH)₂ was used irrespective of the amount of Te. Although the Te⁻ beam intensity gradually decreased as time progressed, the integration of total ion beam intensity was proportional to the maximum beam intensity. Therefore, we applied 250 μg of Ba(OH)₂ for all Te isotope analyses in this study.

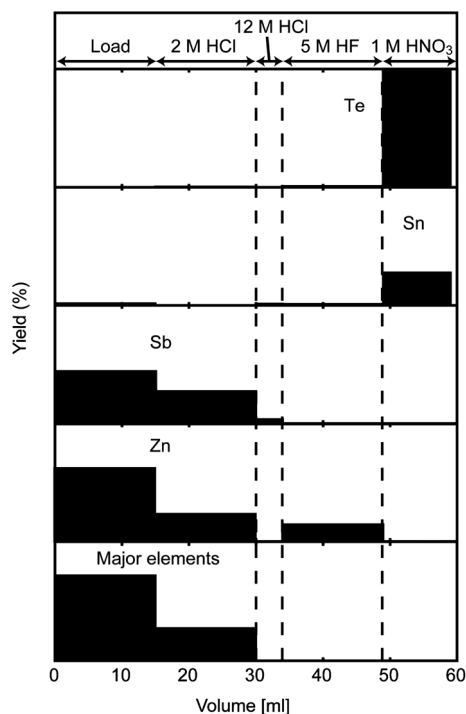


Fig. 1 Elution profiles of Te, Sn, Sb, Zn, and major elements (e.g., Fe and Al) in the first column chemistry step. The horizontal axis represents the total volume of reagents used.

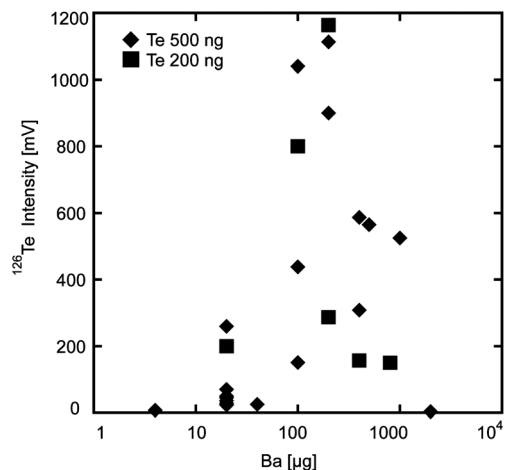


Fig. 2 Relationship between the Te^- beam intensity and the amount of activator loaded onto the filament. Diamond and square symbols represent the data obtained by using 200 ng and 500 ng of Te, respectively.

3.2.2 Filament temperature. Next, we evaluated the optimum filament temperature to obtain the maximum Te beam intensity. The Te^- beam intensity gradually increased as the filament current increased, but it started to decrease when the filament temperature exceeded 890 °C. The typical $^{126}\text{Te}^-$ beam intensity was 200 mV at 800 °C and 600 mV at 850 °C when 200 ng of Te was loaded. At filament temperatures below 800 °C, the beam intensity was stable and did not decrease for 2 h. In contrast, the beam intensity gradually decreased by 60% over 2 h when the filament temperature was maintained in the range 810–860 °C. Nevertheless, we observed that the analytical precision of single Te isotope analysis was better in the latter case: 2SD of the $^{126}\text{Te}/^{128}\text{Te}$ ratios in one run measurement was 85 ppm in the former case and 50 ppm in the latter case. This is because the integrated total ion beam intensity was approximately twice as large in the latter case. The beam intensity rapidly decreased and was not maintained for 2 h when the filament temperature was greater than 890 °C. We concluded that Te isotope analysis should be started in the temperature range of 810–860 °C, where the beam intensity initially grows slightly.

3.3. Evaluation of analytical uncertainty

Fig. 3 shows the $^{126}\text{Te}/^{128}\text{Te}$ ratios of individual cycles in a Faraday cup measurement for our in-house standard (200 ng). The gray circles represent the ratios obtained in individual measurement cycles after mass fractionation correction. The $^{126}\text{Te}^-$ ion beam intensity is plotted as light green symbols. Because the Te^- ion beam intensity gradually decreases during data acquisition, the isotope ratios of individual cycles become more scattered at the end of the measurement compared with the beginning. Therefore, the standard deviation of each block increases in the later blocks. Because we applied the amplifier rotation system of TRITON-plus, a simple average of all cycles with a 2s rejection may provide incorrect data with

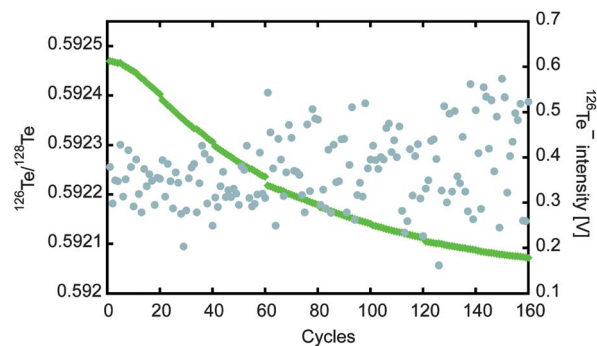


Fig. 3 Variation in $^{126}\text{Te}/^{128}\text{Te}$ ratios and Te ion beam intensity in a single isotope run using Faraday cups. Gray symbols represent $^{126}\text{Te}/^{128}\text{Te}$ ratios for individual cycles.

inappropriate analytical uncertainty by selectively rejecting the data in later blocks.

To avoid this issue, for Faraday cup measurements, we first performed the 2s rejection (up to 10%) for individual blocks (20 ratios). After rejection, the mean of all ratios except rejected data was calculated without further rejection. Fig. 4 shows the $^{126}\text{Te}/^{128}\text{Te}$ ratios in repeated analyses of our in-house standard. Error bars of individual data points are 2 standard errors. The bold line and the shaded zone are the average of 14 runs and its 2 standard deviations, respectively. It is important to note that the standard error of a single run is always much smaller than the reproducibility (2s) of multiple standard runs. Therefore, we prefer the 2s of standard runs as the analytical uncertainty for Te isotope analysis by N-TIMS.

3.4. Determination of dead time for the ion counting system

Isotope ratios obtained by the ion counting system are required to correct the dead time (τ) of the detector. The ion signal loss is emphasized as the rate of ions arriving at the detector increases. For Te, relatively abundant isotopes such as ^{128}Te and ^{130}Te are more affected by the dead time. The correlation between the

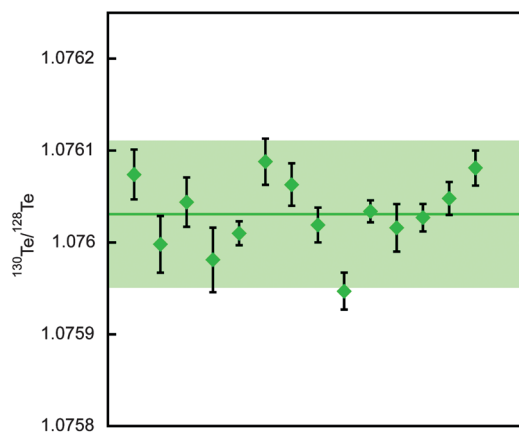


Fig. 4 $^{130}\text{Te}/^{128}\text{Te}$ ratios of individual runs for our in-house standard. The light green line and colored area are an average of 14 runs and 2s, respectively.

observed count rate (N_{obs}) and the true count rate (N_{true}) is given by

$$N_{\text{true}} = \frac{N_{\text{obs}}}{1 - N_{\text{obs}}\tau}. \quad (1)$$

To determine the dead time of the detector on the TRITON *plus* at Tokyo Tech, we measured the Te isotope ratios of our in-house standard solution using the SEM by varying the ion beam intensities and compared the result with those obtained in the Faraday cup runs. Fig. 5 shows the observed $^{130}\text{Te}/^{128}\text{Te}$ ratios in the SEM runs against the ion beam intensity of $^{130}\text{Te}^-$. The obtained isotope ratios are expressed as delta notations defined by the following equation:

$$\delta^{130}\text{Te}_{\text{SEM}} = [(^{130}\text{Te}/^{128}\text{Te})_{\text{SEM}} / (^{130}\text{Te}/^{128}\text{Te})_{\text{Faraday}} - 1] \times 10^{-3}. \quad (2)$$

The $(^{130}\text{Te}/^{128}\text{Te})_{\text{SEM}}$ ratio was recalculated by changing the SEM dead time from 17 ns to 23 ns, which are plotted as

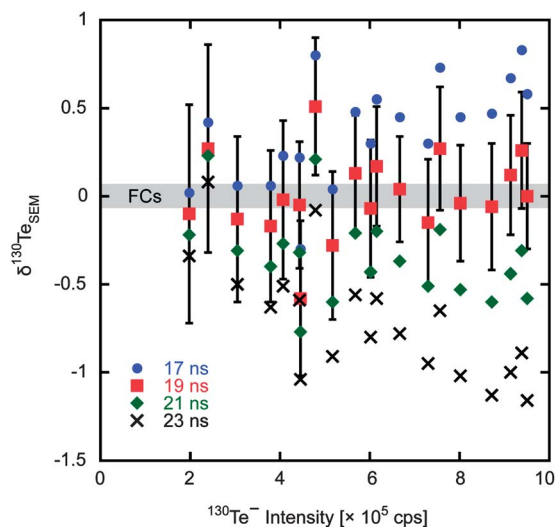


Fig. 5 $^{130}\text{Te}/^{128}\text{Te}$ ratios in delta notation obtained in SEM mode, calculated by varying the SEM dead time (17, 19, 21, and 23 ns). Gray bar indicates the 2s of the Faraday cup measurement.

different symbols in Fig. 5. The gray bar in this figure represents the reproducibility of $(^{130}\text{Te}/^{128}\text{Te})_{\text{Faraday}}$ values (2SD). As observed in Fig. 5, the $\delta^{130}\text{Te}_{\text{SEM}}$ value is identical to zero irrespective of the dead time when the $^{130}\text{Te}^-$ intensity was less than 4×10^5 cps, but it deviates from zero as the beam intensity increases when $\tau = 17$ and 23 ns. In the case of $\tau = 17$ ns, $\delta^{130}\text{Te}_{\text{SEM}}$ becomes positive as the ion intensity increases, whereas it becomes negative when $\tau = 23$ ns. This is clearly caused by an invalid correction of the SEM dead time, because a correction using a dead time larger than the true value overestimates the total number of ions reaching the detector, whereas a smaller dead time underestimates the number of ions. In contrast, $^{130}\text{Te}/^{128}\text{Te}$ is constant irrespective of the $^{130}\text{Te}^-$ beam intensity in the case of $\tau = 19$ ns, strongly suggesting that this is the correct dead time for the SEM. Furthermore, the wrong dead times of 23, 21, and 17 ns cause erroneous corrections for the $^{124}\text{Te}/^{128}\text{Te}$ ratio, which would provide erroneous mass fractionation factors that affect all isotope ratios when the beam intensity is strong. Therefore, we accepted $\tau = 19$ ns as the dead time of the SEM in this study.

3.5. Te Isotope compositions in standard solution

The Te isotope data of our in-house standard generally show good agreement with various terrestrial standards (Johnson Matthey Chemicals, USA and Alfa Aesar, Germany) that were measured in previous studies using MC-ICP-MS^{15,16} (Table 3). It should be noted that the $^{123}\text{Te}/^{128}\text{Te}$ ratio measured in this study was lower than the ratio reported in previous studies using MC-ICP-MS^{15,16} exceeding the analytical uncertainties. This difference was most likely caused by mass interference of $^{123}\text{Sb}^+$ in the ICP-MS measurement, from Sb that was present in the standard solution as an impurity. An $^{123}\text{Sb}^-$ ion beam was not observed using N-TIMS in this study because of the lower ionization efficiency of Sb. Because complete separation of Sb from Te in the column chemistry is difficult to achieve, this feature is one of the advantages of N-TIMS over MC-ICP-MS in Te isotope analysis.

Table 3 Comparison of Te isotope compositions of standard solutions in this study (N-TIMS) and previous studies (MC-ICP-MS)^a

Method	$^{120}\text{Te}/^{128}\text{Te}$	$^{122}\text{Te}/^{128}\text{Te}$	$^{123}\text{Te}/^{128}\text{Te}$	$^{125}\text{Te}/^{128}\text{Te}$	$^{126}\text{Te}/^{128}\text{Te}$	$^{130}\text{Te}/^{128}\text{Te}$	<i>n</i>
This study (Kanto Chemical) N-TIMS FCs ^b	0.002901 ± 25	0.079648 ± 28	0.027865 ± 18	0.222011 ± 22	0.592222 ± 26	1.076120 ± 71	16
This study (Kanto Chemical) N-TIMS FCs ^c	0.002901 ± 18	0.079645 ± 24	0.027865 ± 17	0.222009 ± 21	0.592218 ± 30	1.076048 ± 105	9
This study (Kanto Chemical) N-TIMS FCs ^d	0.002901 ± 31	0.079650 ± 34	0.027865 ± 12	0.222011 ± 29	0.592223 ± 40	1.076029 ± 90	14
This study (Kanto Chemical) N-TIMS SEM	0.002901 ± 19	0.079668 ± 143	0.027852 ± 103	0.221950 ± 223	0.592206 ± 876	1.076371 ± 1398	12
Lee and Halliday (Johnson Matthey) FCs	0.002919 ± 12	0.079603 ± 16	0.027904 ± 12	0.222041 ± 25	0.592264 ± 34	1.075950 ± 30	
Fehr <i>et al.</i> (Alfa Aesar) FCs	0.002896 ± 13	0.079650 ± 11	0.027913 ± 26	0.222003 ± 16	0.592196 ± 26	1.076148 ± 53	

^a Uncertainties are 2s. All Te isotope ratios are normalized to $^{124}\text{Te}/^{128}\text{Te} = 0.14853$ using the exponential law. ^b October 2010G–August 2011.

^c November 2011G–April 2012. ^d February 2013G–July 2013.

The analytical precision of the Te isotope measurement by N-TIMS was roughly the same as that of MC-ICP-MS. The amount of Te required for single isotope analysis by N-TIMS is roughly equal to that of the MC-ICP-MS measurement. The N-TIMS measurement in this study takes approximately 2 h (3 h including the filament heating procedure), whereas the acquisition time is only 10 min for MC-ICP-MS analysis.¹⁶ However, MC-ICP-MS requires thorough washing of the sample introduction system between individual isotope runs to avoid cross-contamination. Additionally, MC-ICP-MS usually applies the sample–standard bracketing protocol to improve the precision and accuracy of isotope data, which increases the total analytical time. Therefore, the running time of N-TIMS is less inferior to the MC-ICP-MS measurement than is generally suggested.

3.6. Long-term reproducibility

We have evaluated the long-term stability of Te isotope ratios using our in-house standard, because fluctuation of Sr isotope ratios measured by the same instrument was observed in previous studies.¹⁸ The fluctuation of Sr isotope ratios is most likely caused by the deterioration of Faraday cups after long-term accumulation of strong ion beams. To evaluate this, the in-house standard was repeatedly measured during the course of this study (from October 2010 to July 2013). Table 3 shows the results of standard runs with 200 ng and 200 pg Te, which were performed by Faraday cups (static mode) and SEM (jumping mode), respectively. As shown in Table 3, the Te isotope ratios measured by FCs in three different analytical periods are in good agreement with each other within the analytical uncertainties. This indicates that the fluctuation of Te isotope ratios is not significant compared to the case of Sr isotope analysis. However, a fluctuation was observed in $^{130}\text{Te}/^{128}\text{Te}$ ratios for which the analytical uncertainty becomes approximately 1.6 times worse when all the data measured in the entire analytical period are averaged (Fig. 6). A possible explanation for this fluctuation is deterioration of the FC (H2) that was used for

collecting approximately 20 V of $^{88}\text{Sr}^+$ ion beam. The $^{130}\text{Ba}^-$ ion beam intensity was less than the detection limit measured by the SEM in some test runs, which were conducted by loading only $\text{Ba}(\text{OH})_2$ on the filament. The $\text{Ba}(\text{OH})_2$ solution was renewed every 3–4 months, and the fluctuation was not correlated with the timing of the change of the $\text{Ba}(\text{OH})_2$ solution. Therefore, the Te isotope data measured by Faraday cups were divided into three groups based on analytical periods (October 2010–August 2011, October 2011–April 2012, and February 2013–July 2013). Consequently, the average reproducibilities in the three analytical periods for each Te isotope ratio were 0.9%, 0.04%, 0.06%, 0.01%, 0.005%, and 0.008% for $^{120}\text{Te}/^{128}\text{Te}$, $^{122}\text{Te}/^{128}\text{Te}$, $^{123}\text{Te}/^{128}\text{Te}$, $^{125}\text{Te}/^{128}\text{Te}$, $^{126}\text{Te}/^{128}\text{Te}$, and $^{130}\text{Te}/^{128}\text{Te}$, respectively.

On the other hand, the Te isotope ratios measured by SEM do not show long-term fluctuation. These ratios are consistent with those measured by Faraday cups within analytical uncertainties. The long-term reproducibility of isotope analysis using Faraday cups was roughly the same as that of MC-ICP-MS. The long-term reproducibility of the SEM measurement was approximately ten times worse than that of Faraday cup runs, except for $^{120}\text{Te}/^{128}\text{Te}$. Because of the extremely low abundance of ^{120}Te , the reproducibility of the $^{120}\text{Te}/^{128}\text{Te}$ ratio measured by SEM was comparable to that measured by Faraday cups.

3.7. Multidynamic collection for $^{126}\text{Te}/^{128}\text{Te}$

Deterioration of Faraday cups may cause long-term fluctuations in isotope ratio measurements. The extent of cup deterioration is evaluated as the “Faraday cup efficiency” defined by the following equation:

$$V = I\alpha R, \quad (3)$$

where V , I , α , and R represent the measured voltage, the electric current of the ion beam, the cup efficiency and the resistance of the amplifier, respectively. The cup efficiency is considered to decrease after extended use of the instrument, and the variation in individual cup efficiencies from the original values strongly depends on the total ion currents accumulated in the cup. Therefore, isotope ratios obtained by the Faraday cup run gradually change as individual cups develop different efficiencies. It should be noted that the Faraday cup efficiencies cannot be determined by the gain calibration of Faraday cup amplifiers. Therefore, renormalization of the isotope ratios based on the repeated analyses of a standard is indispensable for Faraday cup measurements in the static mode.

Multidynamic collection is a powerful approach for reducing the uncertainty of Faraday cup efficiencies. In this study, we applied multidynamic collection to determine the $^{126}\text{Te}/^{128}\text{Te}$ ratio because of the importance of this ratio in ^{126}Sn – ^{126}Te chronology. Assuming that the gain factors of Faraday cup amplifiers are accurately calibrated, Te isotope ratios measured by the Faraday cup setting described in Table 2 are expressed as follows:

$$\left(\frac{^{126}\text{Te}}{^{128}\text{Te}}\right)_{\text{obs}} = \frac{V_{126(1)}\alpha_{\text{H2}}}{V_{128(1)}\alpha_{\text{C}}}, \quad (4)$$

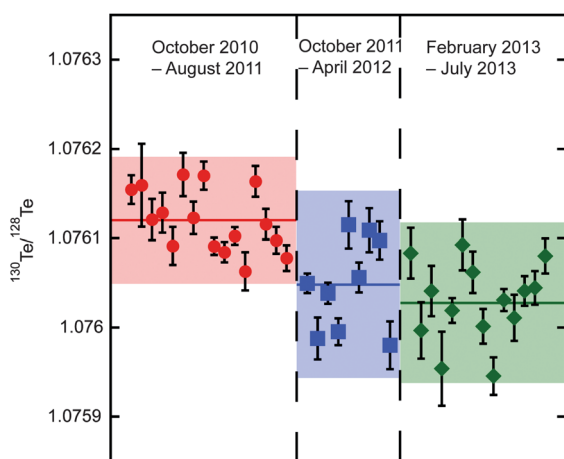


Fig. 6 $^{130}\text{Te}/^{128}\text{Te}$ ratios of our in-house standard measured by the FCs in the course of this study. Data are divided into three groups based on the analytical periods (red: October 2010–August 2011, blue: October 2011–April 2012, and green: February 2013–July 2013).

$$\left(\frac{^{124}\text{Te}}{^{126}\text{Te}}\right)_{\text{obs}} = \frac{V_{124(2)}\alpha_{\text{H2}}}{V_{126(2)}\alpha_{\text{C}}} \quad (5)$$

The subscripts (1) and (2) represent Faraday cup settings. Correction of mass fractionation *via* the exponential law can be described as:

$$\left(\frac{^{126}\text{Te}}{^{128}\text{Te}}\right)_{\text{true}} = \left(\frac{^{126}\text{Te}}{^{128}\text{Te}}\right)_{\text{obs}} \left\{ \frac{(^{124}\text{Te}/^{128}\text{Te})_{\text{true}}}{(^{124}\text{Te}/^{126}\text{Te})_{\text{obs}} \times (^{126}\text{Te}/^{128}\text{Te})_{\text{obs}}} \right\}^f \quad (6)$$

$$f = \frac{\ln(m_{126}/m_{128})}{\ln(m_{124}/m_{128})} \quad (7)$$

where m_n represents the mass of ^nTe .

From these equations, we obtain the following:

$$\left(\frac{^{126}\text{Te}}{^{128}\text{Te}}\right)_{\text{true}} = \frac{V_{126(1)}}{V_{128(1)}} \left\{ \frac{(^{124}\text{Te}/^{128}\text{Te})_{\text{true}}}{(V_{124(2)}/V_{126(2)}) \times (V_{126(1)}/V_{128(1)})} \right\}^f (\alpha_{\text{H2}})^{1-2f} (\alpha_{\text{C}}) \quad (8)$$

It is noteworthy that eqn (8) still has a term containing Faraday cup efficiencies (α_{C} and α_{H2}). However, the value of $(1 - 2f)$ is 0.008 in this case, and the last term in eqn (8) becomes close to 1. This implies that $(\alpha_{\text{H2}}/\alpha_{\text{C}})^{1-2f}$ in eqn (8) can be neglected in the multidynamic collection.

Fig. 7 shows the $^{126}\text{Te}/^{128}\text{Te}$ ratios of our in-house standard measured during the course of this study, which are calculated by static collection (A) and multidynamic collection (B). The average values of (A) and (B) are consistent within analytical uncertainties. However, the 2s of the $^{126}\text{Te}/^{128}\text{Te}$ ratio for (B)

(34 ppm) is 1.6 times better than that for (A) (54 ppm). The definitive influence of the difference in cup efficiencies was not observed during the period of this study. However, if Faraday cups were to deteriorate further, the difference in the $^{126}\text{Te}/^{128}\text{Te}$ ratio between (A) and (B) would be more evident.

3.8. Application of the method

Te is an intriguing element for the study of nucleosynthetic isotope anomalies in meteorites. Some nucleosynthetic isotope anomalies were reported in presolar nanodiamonds from the Allende meteorite,^{9,10} and small potential nucleosynthetic anomalies were observed in Allende CAI.¹⁹ As noted above, the $^{126}\text{Te}/^{128}\text{Te}$ ratio can be used as a short-lived chronometer.

Te isotope compositions in two carbonaceous chondrites and one terrestrial standard rock measured by N-TIMS are reported in Table 4. The results are represented as delta notations, which were normalized to our in-house standard measured during the same analytical period. All the isotope measurements by Faraday cups were obtained in static mode, except for the $^{126}\text{Te}/^{128}\text{Te}$ ratio for which the multidynamic data are additionally reported.

Te isotope compositions in all the terrestrial and extraterrestrial samples were identical to those of the standard within the analytical uncertainty. The results of the two meteorites were consistent with the previous values.⁸ Specifically, ^{126}Te excess was not observed in Allende and Murchison within analytical uncertainties although the multidynamic method was applied. We conclude that our new N-TIMS measurement provides reliable data that are comparable to the data obtained

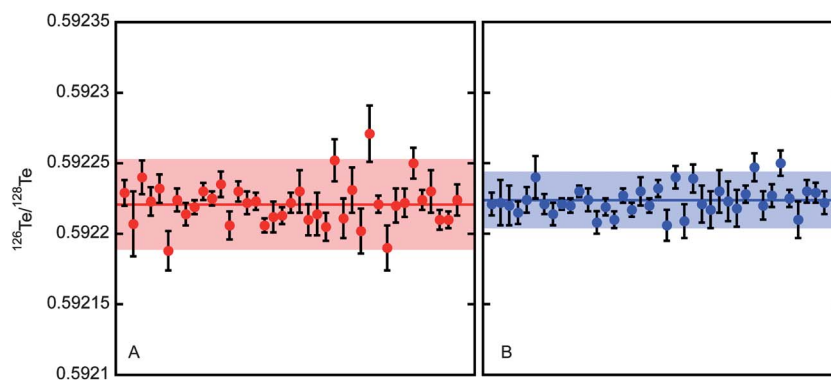


Fig. 7 $^{126}\text{Te}/^{128}\text{Te}$ ratios of our in-house standard measured during the course of this study in (A) static multicollection mode. (B) Multidynamic collection.

Table 4 Te isotope compositions in two chondrites and one terrestrial standard rock sample^{a,b}

Sample	$\delta^{120}\text{Te}$	$\delta^{122}\text{Te}$	$\delta^{123}\text{Te}$	$\delta^{125}\text{Te}$	$\delta^{126}\text{Te}$	$\delta^{126}\text{Te}_{\text{dynamic}}$	$\delta^{130}\text{Te}$
Allende bulk FCs	16.6 ± 13	1.0 ± 0.5	-0.1 ± 0.7	0.4 ± 0.2	0.2 ± 0.1	0.0 ± 0.1	-0.1 ± 0.1
Allende bulk SEM	-1.2 ± 7.7	-0.6 ± 1.9	0.3 ± 3.9	0.5 ± 1.1	-0.1 ± 1.5		0.0 ± 1.5
Murchison bulk FCs	-12.6 ± 22	1.1 ± 1.0	-1.4 ± 1.7	0.3 ± 0.2	0.1 ± 0.1	0.0 ± 0.1	-0.5 ± 0.2
Murchison bulk SEM	0.3 ± 7.7	0.4 ± 2.1	0.6 ± 4.1	0.6 ± 1.2	0.0 ± 1.6		0.3 ± 1.7
JB-3 SEM	-0.8 ± 7.7	0.2 ± 2.1	0.6 ± 4.2	0.3 ± 1.5	-0.1 ± 1.8		-0.3 ± 1.7

^a Uncertainties are 2 standard error of 1 run measurement. ^b All Te isotope ratios are normalized to $^{124}\text{Te}/^{128}\text{Te} = 0.14853$ using the exponential law.

1 by MC-ICP-MS.⁸ However, a more recent report of Te isotope
analysis by a new generation MC-ICP-MS shows better uncer-
tainty for similarly sized samples.²⁰ Further improvement in
TIMS analysis of Te isotopes, such as a double spike method,
5 could provide more precise data on geochemical samples.

4. Conclusion

10 We have developed a method for precise determination of Te
isotope ratios by N-TIMS. Furthermore, an improved chro-
matographic separation technique for Te was established in
which a three-step column chemistry procedure utilizing AG1-
X8, TRU-Spec, and CG-71C resins achieved better separation
15 of Te from unwanted elements and organic matter compared
with previous studies. In N-TIMS analysis, the optimum
analytical condition for obtaining a stable and strong Te⁻ ion
beam was observed when a zone-refined Re single filament was
employed with a Ba(OH)₂ activator by maintaining the filament
20 temperature between 810 and 860 °C during isotope
measurement.

To evaluate the analytical performance of N-TIMS, our in-
house Te isotope standard was repeatedly measured in static
multicollection mode using Faraday cups as well as in SEM
jumping mode. To correct the long-term shift of Te isotope
25 ratios in the Faraday cup run with an amplifier rotation system,
we divided the analytical period into three groups in the course
of this study (~3 years). As a result, the average reproducibilities
during the three analytical periods for Te isotope ratios were
0.9%, 0.04%, 0.06%, 0.01%, 0.005%, and 0.008% for
30 ¹²⁰Te/¹²⁸Te, ¹²²Te/¹²⁸Te, ¹²³Te/¹²⁸Te, ¹²⁵Te/¹²⁸Te, ¹²⁶Te/¹²⁸Te,
and ¹³⁰Te/¹²⁸Te, respectively, which are nearly equal to those
obtained by MC-ICP-MS.

In the SEM jumping mode, it is important to calibrate the
SEM dead time. Te isotope ratios measured by SEM did not
35 show long-term fluctuation. Although the reproducibility of the
SEM measurement was approximately 10 times worse than
Faraday cup measurements, that of ¹²⁰Te/¹²⁸Te was comparable
in the two modes because of the extremely low abundance
of ¹²⁰Te.

40 For the determination of the ¹²⁶Te/¹²⁸Te ratio, we performed
multidynamic collection using Faraday cups. Though the
influence of the difference in cup efficiencies was not evident in
the mean value of the ¹²⁶Te/¹²⁸Te ratio during the period of this
study, the reproducibility in the multidynamic collection was
45 1.6 times better than that in the static mode.

The accuracy of our technique was confirmed by analyzing
two carbonaceous chondrites (Allende and Murchison) and one
50 terrestrial standard (JB-3). The Te isotope compositions of two
chondrites were identical to the terrestrial sample within
analytical uncertainties, indicating that these samples possess
no nucleosynthetic isotope anomalies. This result is consistent
with the findings of previous MC-ICP-MS studies.

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