

# Precise and Accurate Mass-independent Chromium Isotope Measurement by Total Evaporation Mode on Thermal Ionization Mass Spectrometry (TE-TIMS) at 200 ng Level

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**ABSTRACT:** Mass-independent chromium (Cr) isotope ratios measurements have been widely used in dating early solar system events and tracing the genetic relationships between different solar system, as well as terrestrial materials. Current analytical techniques need relatively large sample sizes, and this limits the application of Cr isotopes on precious mission return samples and some Cr-poor samples (e.g., BCR-2 with Cr contents of ~15 ppm). This paper reports a novel analytical method for mass-independent Cr isotopic ratios measurements using a Thermal Ionization Mass Spectrometer (TIMS) operated in total evaporation (TE) mode. A three-step cation column (AG 50W-X12 resin, 200–400 mesh) chemistry is used to purify Cr in various samples, including chondrites, basalts and peridotites, and the Cr yield is better than 92%. Residual organics from column resins is detrimental to Cr ionization on filaments, we demonstrate that this can be effectively removed by treating samples with H<sub>2</sub>O<sub>2</sub> at 40 °C on hotplate. Single Cr measurements on rhenium filaments consume 15 to 20 ng of Cr and sustain <sup>52</sup>Cr of ~10V for 10 to 20 minutes. Generally, for one sample of 200 ng Cr, 10–15 ng repeated measurements can be made and 2-standard error precisions of ~0.05 and ~0.10 for ε<sup>53</sup>Cr and ε<sup>54</sup>Cr\*, respectively can be achieved. The reproducibility (the 2-standard deviation) for ε<sup>53</sup>Cr and ε<sup>54</sup>Cr is 0.05 and 0.07, respectively, tested by multiple measurements for DTS-2b (USGS dunite) and NWA 7734 (ordinary chondrite). Concentration and doping test (mainly for Fe) have also been conducted. These tests show that the Fe/Cr must be < 5 % and the measured <sup>56</sup>Fe/<sup>52</sup>Cr < 1 ‰ in order to achieve accurate ε<sup>54</sup>Cr. Finally, the ε<sup>53</sup>Cr and ε<sup>54</sup>Cr values measured by normal method on TIMS are systematically higher than those measured by total evaporation method on TIMS, which is potentially caused by non-kinetic mass-dependent fractionation during Cr evaporation and ionization on TIMS. The TE method could reduce this effect that may cause inaccurate mass-independent Cr isotope data on TIMS.

## INTRODUCTION

Mass-independent chromium (Cr) isotope fractionation plays central in understanding the formation of terrestrial planets and early Solar System evolution. Cr isotopes (mass-independent) are fractionated on radiogenic,<sup>1</sup> nucleosynthetic<sup>2,3</sup> and cosmogenic effects.<sup>4</sup> The short-lived radionuclide <sup>53</sup>Mn, with a half-life of 3.7 ± 0.2 Myrs,<sup>5</sup> decays to <sup>53</sup>Cr and was present in the early Solar

System.<sup>6</sup> Therefore, the <sup>53</sup>Mn-to-<sup>53</sup>Cr decay system is a useful chronometer to date early Solar System events such as chondrule (precursor) formation,<sup>7-10</sup> differentiation of planets/asteroids,<sup>6,8,11-16</sup> as well as chondrite parent body processes.<sup>11,17,18</sup> Injection of Supernova material potentially caused <sup>54</sup>Cr isotopic heterogeneity among different groups of meteorites originating in different regions of the solar protoplanetary disk.<sup>3,19-23</sup> The variation of <sup>54</sup>Cr isotopic anomalies provides a robust means for tracing the kinship

between Solar System materials, including the origin of Earth-Moon system,<sup>24</sup> chondrule formation,<sup>8-10,25,26</sup> terrestrial impact events,<sup>27,28</sup> the relationships between different groups of chondrite (e.g., CV-CK, CB-CH and CO-CM),<sup>23</sup> planetary mantle heterogeneity,<sup>14</sup> and the number of the meteorite parent bodies.<sup>15</sup> The cosmogenic Cr isotope ingrowth is mainly found in the material with high Fe/Cr ratios and long cosmic ray exposure ages, including metal phases in chondrites,<sup>20</sup> iron meteorites<sup>20,29</sup> and lunar samples.<sup>30</sup>

The application of Cr isotopes for unravelling these planetary and cosmochemical issues is based on making both highly precise and highly accurate mass-independent Cr isotope measurements. Thermal ionization mass spectrometry (TIMS) is the technique of choice for mass-independent Cr isotopic ratios measurements<sup>31,32</sup>, as the specificity of ionization in TIMS ion source can effectively avoid the isobaric interferences from <sup>54</sup>Fe on <sup>54</sup>Cr, as well as <sup>50</sup>V and <sup>50</sup>Ti on <sup>50</sup>Cr.<sup>33</sup> However, it appears that there are small residual mass-dependent fractionations that cannot be corrected for. This residual fractionation is evident in the correlation of  $\epsilon^{53}\text{Cr}$  and  $\epsilon^{54}\text{Cr}$  (where  $\epsilon^{53}\text{Cr}$  and  $\epsilon^{54}\text{Cr}$  are the per 10'000 mass-independent isotope deviations in <sup>53</sup>Cr/<sup>52</sup>Cr and <sup>54</sup>Cr/<sup>52</sup>Cr ratios relative to NIST 3112a.) for multiple measurements of standards<sup>20,27,34</sup> which should otherwise show no correlation. In detail, the  $\epsilon^{53}\text{Cr}$  and  $\epsilon^{54}\text{Cr}$  vary from -0.2 to 0.2 and from -0.4 to 0.4, respectively, with a slope of ~2.62 that is confirmed by the theoretical calculation about the slope (2.61) of  $\epsilon^{53}\text{Cr}$  and  $\epsilon^{54}\text{Cr}$  variation based on different Cr oxides and different mass fractionation laws.<sup>23</sup> This apparent mass dependent Cr isotope fractionation during TIMS measurement is explained by the use of an unsuitable correction law (using exponential law) for correcting the mass-dependent equilibrium isotope fractionation between multiple Cr oxide species e.g., CrO and CrO<sub>2</sub>.<sup>23,34</sup> Hence, the effect of different mass fractionation behaviors of Cr and its oxide species greatly hampers both the precision and accuracy of Cr isotope measurements by TIMS. Another problem for Cr isotopes measurements on TIMS is the presence of organics from the ion exchange resins used in the Cr separation. If these organics are not sufficiently broken down (oxidized) following separation, then their presence on the filament has been shown to be deleterious to Cr ionization.

Alongside thermal ionization mass spectrometry mass-dependent Cr isotopes can also be measured by multi-collector inductively coupled plasma mass spectrometry (MC-ICP-MS). Plasma based techniques have the advantage there is no Cr evaporation process during ionization and using samples standard bracketing techniques it MC-ICP-MS has produced higher precisions (~0.03 and ~0.06 for  $\epsilon^{53}\text{Cr}$  and  $\epsilon^{54}\text{Cr}$ , respectively) than those on TIMS (~0.06 and ~0.12 for  $\epsilon^{53}\text{Cr}$  and  $\epsilon^{54}\text{Cr}$ , respectively), when giving same measurement times.<sup>14,15,22,23,35,36</sup> However, due to the poor specificity of the ICP ion source more rigorous chemical purification (e.g., a four-step column chemistry) is needed to separate Cr from matrix elements,

especially the isobaric elements for Cr, *i.e.*, Fe, Ti and V.<sup>23,35,36</sup>

In addition to elemental isobaric interference, mass-independent Cr isotope measurements on MC-ICP-MS also need optimizing to avoid Ar based polyatomic interference on the isotopes of interest, e.g., <sup>40</sup>Ar<sup>12</sup>C (on <sup>52</sup>Cr), <sup>40</sup>Ar<sup>14</sup>N (on <sup>54</sup>Cr) and <sup>40</sup>Ar<sup>16</sup>O (on <sup>56</sup>Fe that is used to correct <sup>54</sup>Fe). Such interferences are typically dealt with by operating the MC-ICP-MS in medium mass resolution ( $m/\Delta m > 5,000$ ) and mass resolving the interference. However, operating in medium mass resolution comes at a cost of sensitivity and mass-independent Cr isotope measurements on MC-ICP-MS and, also the typical TIMS measurements requires at least 500 ng of loading Cr for high-precision measurement,<sup>23,31,36,37</sup> and up to 8-10  $\mu\text{g}$ .<sup>38</sup> This relatively large sample size limits the application of Cr isotopes in some Cr-poor and precious samples. For instance, small samples such as micro-drilled chondrules, chondritic refractory inclusions; low-Cr content samples including tektites, carbonates and Fe-Mn nodules and precious samples from sample return missions, e.g., Chang'E, Hayabusa, Martian Moon eXploration (MMX) and OSIRIS-Rex missions.

The method of total evaporation (TE) on TIMS may be developed for mass-independent Cr isotope measurements. Total evaporation method attempts to evaporate all sample loaded onto the filament over a relatively short period of time and aims to effectively decrease the mass fractionation of a sample. For example, Fiedler et al.<sup>39</sup> reported that the standard deviation of repeated <sup>240</sup>Pu/<sup>239</sup>Pu ratio analyses decreased from 0.038% to 0.008% when TE-TIMS was applied compared to standard measurements. For Cr the TE-TIMS method requires only ~15 ng of Cr and can be run using the single filament configuration. This means that the absolute amount of organics on each filament can be decreased, assuming the amount of residual organics from column separation is independent of the amount sample, and hence the amount of Cr processed. Similar TE-TIMS method for Cr isotope measurements has already been used in previous studies,<sup>10,13,15,26</sup> but the detailed methodology has not been systematically reported. Furthermore, during data acquisition, some of the previous TE-TIMS Cr work calculated the isotope ratios for every measured cycle and then took the mean, rather than calculating the isotope ratios from mean signals over all cycles,<sup>10,13,26</sup> which does not follow the theory of total evaporation.

For mass-independent isotope ratio measurements, the yield of Cr column chemistry should be taken into consideration. This is because a low yield (e.g., < 80%) may result in non-exponential mass-dependent isotope fractionation of Cr and this cannot be corrected for during measurement unless the exact style of the mass-dependent fractionation is known.<sup>31</sup> Here, a high-yield (> 90%) three-step Cr column chemistry is developed that can be used for a variety of samples (e.g., chondrites, basalts and peridotites). Additionally, a novel and effective method for

removing the residual organics from the resin is described, which may also help improve the TIMS method for the mass-dependent Cr isotope fractionation. We report the detailed methodology for mass-independent Cr isotope measurements using TE-TIMS, including the tests for concentration effect and Fe-doping.

## EXPERIMENTAL

**Chemical reagents and materials.** All chemical procedures were carried out in laminar flow hoods (Class 100) in a clean room (Class 1000) with filtered air. Ultrapure water (Milli-Q) with a resistivity of 18.2 M $\Omega$ -cm was used for diluting reagents. All optima-grade grade (BV-III) acids (hydrochloric acid (HCl), nitric acid (HNO<sub>3</sub>) and hydrofluoric acid (HF) which are from Beijing chemical factory), were further purified twice using a sub-boiling distillation system (SavilleX DST-1000 Minnetonka, USA). Boric acid (99.99%) and silicon dioxide (99.99%) with alumina doping are obtained from Sigma-Aldrich (701491). NIST SRM 3112a Cr (1000 ppm) is used as isotopic reference standard whilst GSB-Ti, Fe, V, K, Na, Ca, Mg and Mn ultrapure standard solutions of 1000 ppm are from the China Iron and Steel Research Institute.

PFA beakers (SavilleX) were cleaned with BV-III 7 M HNO<sub>3</sub> and/or 5.5 M HCl for 8 h on a hot plate at 130 °C, followed by distilled 7 M HCl and ultrapure water at 130 °C for 8 h. TIMS filaments (single filament) are made from rhenium ribbon (99.99% purity, 0.014 mm thick, 0.28 mm wide, H. Cross company).

Rock standard samples: rock powders of BHVO-2 (basalt), BCR-2 (basalt), DTS-2b (dunite) were obtained from the United States Geological Survey (USGS), The Rock powders of JP-1 (peridotite) are from Geological Survey of Japan (GSJ). In addition, a carbonaceous chondrite, Murchison [CM2] and an ordinary chondrite, Northwest Africa [NWA] 7734 [H4], Allende [CV3] were also analyzed in this study.

**Sample preparation and digestion.** Sample powders (~50 mg) were digested with concentrated HF (29 M) and HNO<sub>3</sub> (14 M) in PFA beakers at 150 °C on hotplates for more than seven days for most terrestrial geological reference materials (DTS-2b, JP-1) and meteorites samples (Murchison CM2, NWA 7734 [H4]) and then evaporated to dryness. Samples were then redissolved in concentrated aqua regia (HCl:HNO<sub>3</sub> = 3:1) for more than seven days and then evaporated to dryness at 130 °C. The samples were then redissolved in 0.5 ml of concentrated HCl (11 M) afterwards evaporated to dryness on a hot plate at ~100 °C. Finally, the samples were re-dissolved in 0.2 ml 6 M HCl in preparation for column chemistry.

**Column chemistry.** In this study a three step, high Cr yield chromatography procedure is developed using AG 50W-X12

**Table 1.** Two-column procedure for Cr chemical separation on cation-exchange resin

Step	Acid volumes	Acid
<b>Column 1 + 2: AG50W-X12 200 ~ 400 mesh (1 ml resin, 4 mm internal diameter column)</b>		
Wash resin	5 mL	6 M HCl
Wash resin	2 mL	MQ
Pre-condition	3 ml	1 M HCl
Load sample#	1.2 ml	1 M HCl
Collect Cr	3.5 ml	1 M HCl
Elute matrix and collect residual Cr	3 ml	6 M HCl
<b>Column 3: AG50W-X12 200 ~ 400 mesh (0.33 ml resin)</b>		
Wash resin	2 ml	6 M HCl
Wash resin	1 ml	MQ
Pre-condition	1 ml	0.5 M HNO <sub>3</sub>
Load sample#	1 ml	0.5 M HNO <sub>3</sub>
Elute residual Al, Ti	2.5 ml	1 M HF
Elute residual Mg, Na, K	6 ml	1 M HCl
Collect Cr	1.6 ml	6 M HCl

**Note:** Before the column 2, the matrix collected by 3ml 6M HCl should repeat column 1, then the mixed total Cr load together for the column 2.  
#: Before loading samples, we processed the samples with the detailed methods described in section “Column chemistry”.

**Fig. 1** The Cr elution curve of BHVO-2 for column 1 and column 2 using AG50W-X12 resin (200 ~ 400 mesh). The column 1 is 4 mm in diameter and 10 cm in length and column 2 is 4 mm in diameter and 3 cm in length (Table 1). Concentrations of eluting elements were analyzed on Element XR ICP-MS in the Isotope Geochemistry Lab of the China University of Geosciences, Beijing.

(Bio-Rad) resin. AG 50W-X12 resin was used in the chromatography procedure as it as a higher cross-linkage, smaller wet bead size, and smaller molecular weight limits than the Bio-Rad AG50W-X8 (200 ~ 400 mesh), which will give better separation of Cr and Mg.<sup>41</sup> The column chromatography used in this study is described in Table 1 and an example elution curve for the BHVO-2 reference material is shown in Fig. 1.

In order to achieve high Cr yields in column chromatography, it

is essential to control the oxidation state of the Cr in solution. Therefore, prior to loading on the first ion exchange column, samples are refluxed overnight in 0.2 ml of 6 M HCl at 130 °C to promote the formation of Cr<sup>3+</sup>-Cl species (mainly Cr(H<sub>2</sub>O)<sub>5</sub>Cl<sup>2+</sup> / CrCl<sub>3</sub>(H<sub>2</sub>O)<sub>3</sub><sup>0</sup>), which have a low affinity of the cation resin and are eluted early.<sup>33,42</sup> The first column uses 1 ml of AG50W-X12 resin in 4 mm diameter columns. Before loading the samples on the column, the resin was cleaned with 5 ml 6 M HCl and 3 ml MQ water, then conditioned with 3 ml 1 M HCl. Samples, in 0.2 ml 6 M HCl, were diluted to 1 M HCl with 1 ml of ultrapure water then immediately loaded on to columns followed by 3.5 (1 + 1 + 1.5) ml 1 M HCl to collect Cr. In this step, Cr was separated from most major elements, *e.g.*, Fe, Mg, Mn, Ni, and V (Fig. 1). This chromatography also has a good separation of Cr from V and Mg which has been a problem for previous column chromatography using 0.5 M HNO<sub>3</sub> matrices, which have high (99 %) Cr yield but required a fourth TODGA column and still do not achieve adequate V separation on basaltic V-rich matrixes.<sup>23,36,26,42</sup>

In order to improve the chromatography yield for the first column, following the collection of the main ~85% Cr elution the remaining ~15 % Cr and sample matrix was collected using 3 (1 + 1 + 1) ml 6 M HCl.<sup>15</sup> This aliquot was then evaporated at 130 °C to reduce the sample volume and promote CrCl<sub>3</sub>(H<sub>2</sub>O)<sub>3</sub><sup>0</sup> formation and reloaded on to the first column which was cleaned with 5 ml of 6M HCl and reconditioned with 3ml of 1M HCl. In this way, Cr is well separated from V and Mg and a high Cr yield is maintained. The Cr yield is around 97% after the first and second columns. The Cr from these two steps were then recombined and re-digested in 0.5 M HNO<sub>3</sub> before loading on the third column.

As with columns 1 and 2 control over the oxidation state of Cr in solution is critical. Prior the third column samples are dried down three times in 0.1 ml of concentrated HNO<sub>3</sub> to convert to nitrate form. Samples are then redissolved in 250 µl 2 M HNO<sub>3</sub>, and then diluted with 730 µl MQ water to achieve ~1 ml of ~0.5 M HNO<sub>3</sub>. This solution was heated on a hotplate at 130 °C for two hours, in order to promote the formation of Cr<sup>3+</sup> and equilibrium for the different species. After that, 20 µl of 30% H<sub>2</sub>O<sub>2</sub>, is added and the solution kept at room temperature for 48 h, in order to maximise the promotion of Cr<sup>3+</sup>.

The third column contains 0.33 ml of Bio-Rad AG50W-X12 (200 ~ 400 mesh) cation exchange resins.<sup>41</sup> The resin was cleaned with 2 ml 6 M HCl and 1 ml MQ water, then preconditioned with 1 ml 0.5 M HNO<sub>3</sub>. Samples are loaded in 1 ml 0.5 M HNO<sub>3</sub>, followed by 2.5 ml (1 + 1.5) 1 M HF to effectively remove residual Ti, Al, Fe and V, and 6 (3 + 3) ml 1 M HCl to remove remaining Mg, K and Ca, and Na. Finally, Cr was collected with 1.6 (0.4 + 0.4 + 0.4) ml 6 M HCl. The yield of this column is higher than 95%. Compared to 3 ml 6 M HCl for final Cr collection with the same columns in previous study,<sup>31</sup> less acid is used in this step and this should lead to less organics in the sample from the resin, but also will not lose Cr.

**Table 2.** Cup configuration for Cr isotope analysis

Element	L4	L2	L1	C	H1	H2	H3
Cr	<sup>49</sup> Ti	<sup>50</sup> Cr	<sup>51</sup> V	<sup>52</sup> Cr	<sup>53</sup> Cr	<sup>54</sup> Cr	<sup>56</sup> Fe

The total recovery of Cr for diverse samples from the three-column cation-exchange chromatography procedure is higher than 90%. For example, the total Cr recovery for BCR-2 ([Cr] = 15 ppm), BHVO-2 ([Cr] = 280 ppm), and DTS-2b ([Cr] = 15500 ppm) of this study are 92%, 92%, and 98%, respectively. Total chemistry blanks for the column separation procedures are less than 0.5 ng, which are negligible compared to more than 200 ng quantities of Cr isolated from each sample of this study.

**Thermal ionization mass spectrometry-Total Evaporation (TE).** Chromium isotope ratios were analyzed on a Thermo Fisher Scientific TRITON Plus (TIMS) in the Isotope Geochemistry Lab of the China University of Geosciences, Beijing. Samples were loaded on outgassed Re filaments and narrow parafilm dams were used on the Re filaments to constrain the samples solution while loading, which was performed at 1 A current. Samples were loaded as 1 µl containing 15 ng of Cr and a further 1 µl of mixture of Al-bearing silica gel and concentrated H<sub>3</sub>BO<sub>3</sub> (1:1) was then loaded the mixture was then dried by heating quickly to 1.5 A, and then increase the current to ~2.2 A until the filament showing dull red for 1 s to form a glass. We have tested that compared to the typical slow drying at 0.5 A current,<sup>33</sup> and the fast drying in this study will not affect the final Cr data.

During a measure procedure, total evaporation (TE) mode was chosen in the method file. The cup configuration for Cr isotope measurements is listed in Table 2. The following parameters are set: idle time of 3 s; heat-slope of 3 mA/cycle; the pilot signal (on <sup>52</sup>Cr) of 10000 mV; number of cycles 1960 and an integration time of 1.049 s. No baseline measurements were taken during measurement as this will result in lost signal and compromise the total evaporation. In fact, we process the data in the TE mode, *i.e.*, calculate the sum of the signals from all measurement cycles. Compared to the sum of all the signals, *e.g.*, ~3000 V for <sup>54</sup>Cr (the Cr isotope with the lowest abundance), the noise of faraday cups (mostly lower than 10<sup>-5</sup> V) can be neglected. Isobaric interferences from Ti<sup>+</sup> and V<sup>+</sup> and Fe<sup>+</sup> on Cr<sup>+</sup> were corrected assuming natural isotope ratios, <sup>49</sup>Ti/<sup>50</sup>Ti = 1.0185, <sup>51</sup>V/<sup>50</sup>V = 399.0 and <sup>56</sup>Fe/<sup>54</sup>Fe = 15.698, and the mass-dependent Cr isotope fractionation from the instrument and column were all normalized by <sup>50</sup>Cr/<sup>52</sup>Cr = 0.051859 using an exponential law.<sup>6,43</sup>

All the measurements were run automatically in a sequence that includes 21 filaments. In detail, six NIST 3112a filaments and three other samples of five individual filaments are run in a day with a NIST 3112a filaments run for every three sample filaments. Sequences were started after a five-hour pump down, when the source pressure is lower than 5 × 10<sup>-7</sup> Pa, without using any liquid nitrogen to further increase the vacuum. The automatic filament

**Table 3.** Reported methods for organic component eliminated of Cr by TIMS

Material used	Methods	Reference
H <sub>2</sub> O <sub>2</sub>	100 µl of H <sub>2</sub> O <sub>2</sub> to dryness and purple at 40 °C	This study
HNO <sub>3</sub>	100 µl of concentrated HNO <sub>3</sub> for three times	Zhu <i>et al.</i> <sup>15</sup> ; Qin <i>et al.</i> <sup>20</sup>
HClO <sub>4</sub> + HNO <sub>3</sub>	two weeks at room temperature	Liu <i>et al.</i> <sup>39</sup>
Ultraviolet radiation/H <sub>2</sub> O <sub>2</sub>	100 µl of 30% H <sub>2</sub> O <sub>2</sub> to dryness at 70 °C	Johnson and Bullen <sup>43</sup>
H <sub>2</sub> O <sub>2</sub> + HNO <sub>3</sub>	100 µl of H <sub>2</sub> O <sub>2</sub> and 100 µl of HNO <sub>3</sub>	Chrastny <i>et al.</i> <sup>47</sup>
Aqua regia + HNO <sub>3</sub>	aqua regia for one week and HNO <sub>3</sub> for three days	Van Kooten <i>et al.</i> <sup>26</sup>

heating program increases the stable <sup>52</sup>Cr<sup>+</sup> beams to 6 V (we set automatic signal tuning at 0.01 V and 1 V for <sup>52</sup>Cr beam), and finally the measurement will also stop when the signal decreases below 6 V. Each sample was analyzed for 10 – 15 times (with 10 – 15 filaments, and each filament is only for one measurements), until the 2SE uncertainties for ε<sup>53</sup>Cr and ε<sup>54</sup>Cr are lower than or close to ~0.05 and ~0.10, respectively, and typical 15 ng Cr loads of NIST 3112a or from sample purification usually achieves 800 ~ 1800 cycles of data.

For data collection, measurements with less than 600 cycles are not considered and <sup>56</sup>Fe/<sup>52</sup>Cr ratio > 1 × 10<sup>-3</sup> (see discussion in the doping test later) are not considered valid. The final sum <sup>53</sup>Cr/<sup>52</sup>Cr and <sup>54</sup>Cr/<sup>52</sup>Cr ratios (sum of total 800 ~ 1960 cycles) is used to calculate epsilon Cr values, which is different from the previous studies using the mean <sup>53</sup>Cr/<sup>52</sup>Cr and <sup>54</sup>Cr/<sup>52</sup>Cr ratios of each cycle.<sup>9,10,26</sup> Considering the mass-dependent fractionation on the TIMS, we calculate the sample data relative to the mean of the NIST 3112a measurements (n = 6) in a same turret. All the <sup>53</sup>Cr/<sup>52</sup>Cr and <sup>54</sup>Cr/<sup>52</sup>Cr ratios of the samples are expressed as the epsilon notations relative to the reference material NIST 3112a:

$$\epsilon x_{Cr} = \left( \frac{\left( \frac{x_{Cr}}{^{52}Cr} \right)_{\text{sample}}}{\left( \frac{x_{Cr}}{^{52}Cr} \right)_{\text{NIST3112a}}} - 1 \right) \times 10000 \quad (1)$$

where x = 53 or 54.

**Minimizing of organic matter.** Organics from the column resin has always been considered to be a significant impediment for obtaining stable Cr ionization on TIMS.<sup>33,37,44,45</sup> Although less acid was used in the third-column Cr collecting step (see section “Column chemistry”) and total evaporation method (see section “Thermal ionization mass spectrometry-Total Evaporation (TE)”) can effectively reduce the amount of organics introduced onto the filaments, further reduction in organics can be achieved by chemical treatment of the sample following chromatography. Perchloric acid (HClO<sub>4</sub>), ultraviolet radiation, aqua regia, HNO<sub>3</sub>, or H<sub>2</sub>O<sub>2</sub> are usually used to eliminate organic matter<sup>20,23,26,41,45</sup> (Table 3). The HClO<sub>4</sub> is a strong acid, and a powerful oxidizer when hot, which should effectively oxidize and remove the organics. However, the HClO<sub>4</sub> may result in loss of Cr by forming volatile CrO<sub>2</sub>Cl<sub>2</sub> during the subsequent evaporation to dryness, as

the boiling point temperature of CrO<sub>2</sub>Cl<sub>2</sub> is significantly less than the temperature required to effectively evaporate HClO<sub>4</sub>.<sup>44,46,47,48</sup> Liu *et al.*<sup>41</sup> used 30 µl of HClO<sub>4</sub> and 500 µl of HNO<sub>3</sub> to effectively eliminate organic matter at low temperature and avoided the volatilization of CrO<sub>2</sub>Cl<sub>2</sub>. However, it needs long time (two weeks). Also considering the explosive risk for HClO<sub>4</sub> at high temperatures, this method is not recommended. Van Kooten *et al.*<sup>26</sup> used concentrated aqua regia followed by concentrated HNO<sub>3</sub> to remove the organics in Cr from the column and needed about 10 days.

We have also tested HNO<sub>3</sub> and H<sub>2</sub>O<sub>2</sub> for their ability to remove the organics from Cr solutions following chemistry. We have found that repeated evaporation to dryness in concentrated HNO<sub>3</sub> and heat the samples in concentrated HNO<sub>3</sub> (1ml) overnight are insufficient to totally remove organics. We observe in Cr-poor samples such as BHVO-2 and BCR-2, where organics are not as effectively diluted on when loading onto filament, the Cr ion beams on TIMS are have low intensity and rapidly decrease. H<sub>2</sub>O<sub>2</sub> is widely used when digesting organic matter for isotope measurements. Johnson and Bullen<sup>45</sup> firstly employed H<sub>2</sub>O<sub>2</sub> on a 70 °C hot plate, under ultraviolet rays for decomposing H<sub>2</sub>O<sub>2</sub>. Although the relatively high temperature could potentially increase the oxidative ability, we found 70 °C also increase the speed of decomposition of H<sub>2</sub>O<sub>2</sub>, which intensively generates oxygen bubbles. The breaking of these bubbles could splash the sample outside of the beakers. Since we found that H<sub>2</sub>O<sub>2</sub> alone can effectively remove organics, it is not necessary to use ultraviolet rays for decomposing the H<sub>2</sub>O<sub>2</sub> to H<sub>2</sub>O and O<sub>2</sub> and hence we did not follow this method. In this study, 100 µl of H<sub>2</sub>O<sub>2</sub> was used to eliminate organic compounds with low temperature, i.e., 40 °C for two-three hours which prevented rapid decomposition of the H<sub>2</sub>O<sub>2</sub> and sample splash. During the process, the Cr solution are observed to turn purple in colour that could be due to the oxidation of Cr to CrO<sub>4</sub><sup>2-</sup>. After drying down the H<sub>2</sub>O<sub>2</sub>, samples are redissolved in 0.5 ml conc. HCl to reduce the Cr to Cr<sup>3+</sup>. Following the H<sub>2</sub>O<sub>2</sub> treatment signals for the solution standards, geological reference materials and meteorites (15 ~ 20 ng Cr) are all stable at 10 V for 1000 ~ 1800 cycles (integration time of 1.049 s) after above eliminating organics procedure.

Another way to minimize the organics is using a tiny column with less resin, which will introduce less organics from the resin.<sup>13</sup> All the organics affecting the Cr ionization should from the last wash

**Table 4.** The  $\epsilon^{53}\text{Cr}$  and  $\epsilon^{54}\text{Cr}$  for the mixture of NIST 3112a and GSB Fe with different Fe/Cr ratios (0.01 ~ 1)

Fe doping	$^{56}\text{Fe}/^{52}\text{Cr}$ (measured)	$\epsilon^{53}\text{Cr}$	2SD	2SE	$\epsilon^{54}\text{Cr}$	2SD	2SE	N
Fe/Cr = 1/100	0.0002	0.02	0.18	0.05	-0.01	0.37	0.10	14
Fe/Cr = 1/20	0.0009	-0.02	0.22	0.06	0.01	0.42	0.11	14
Fe/Cr = 1/10	0.0024	0.04	0.19	0.06	0.32	0.34	0.11	9
Fe/Cr = 1/2	0.0082	0.04	0.10	0.03	0.63	0.33	0.11	9
Fe/Cr = 1	0.017	0.05	0.18	0.05	1.11	0.49	0.13	14

## RESULTS AND DISCUSSION

**Isobaric interference and doping test.** Fe, Ti, and V are the major isobaric interferences on the isotopes of Cr ( $^{54}\text{Fe}$ - $^{54}\text{Cr}$  and  $^{50}\text{V}$ - $^{50}\text{Cr}$ ). However, Ti and V have high first ionization potentials, and are typically not ionized under the same conditions as Cr with the emitters of silica gel and  $\text{H}_3\text{BO}_3$  by TIMS.<sup>39,46</sup> In addition, our three-step column chromatography procedure provides an effective separation of Cr from Ti and V, hence we do not perform doping tests for Ti and V. However, Fe is a major element and rich in both rock samples and the environment (causing a high Fe in blank), and Fe can be ionized in the presence of silica gel and  $\text{H}_3\text{BO}_3$  emitters at slightly higher temperature ( $> 1350\text{ }^\circ\text{C}$ )<sup>41</sup> than that of Cr which is usually between  $1100\text{ }^\circ\text{C}$  and  $1400\text{ }^\circ\text{C}$ . Therefore, it is still important to examine the potential influence of isobaric interference from  $^{54}\text{Fe}$  on  $^{54}\text{Cr}$  with the total evaporation of TIMS. The  $\epsilon^{53}\text{Cr}$  and  $\epsilon^{54}\text{Cr}$  values on a mixture of NIST SRM 3112a and GSB Fe were analyzed for the Fe/Cr ratios ranged from 0.001 to 1. As shown in the Table 4 and Fig. 2, the  $\epsilon^{53}\text{Cr}$  values of these mixtures with different Fe/Cr ratios are identical within our precision ( $-0.02 \pm 0.06 \sim 0.02 \pm 0.06$ , 2 SE,  $n = 9\text{-}14$ ), so addition of Fe has no effect on  $\epsilon^{53}\text{Cr}$  data. However,  $\epsilon^{54}\text{Cr}$  values of these mixtures are increases with higher Fe/Cr, which are range from  $-0.01 \pm 0.10$  ( $^{56}\text{Fe}/^{52}\text{Cr} = 0.0002$ ) to  $1.11 \pm 0.13$  ( $^{56}\text{Fe}/^{52}\text{Cr} = 0.017$ ) caused by the isobaric interference from  $^{54}\text{Fe}$  on  $^{54}\text{Cr}$  after corrected by isobaric interferences from  $\text{Fe}^+$  on  $\text{Cr}^+$  with  $^{56}\text{Fe}/^{54}\text{Fe} = 15.698$  as that of other samples. From these data, it is clear that interference from  $^{54}\text{Fe}$  on  $^{54}\text{Cr}$  can be sufficiently corrected for when  $^{56}\text{Fe}/^{52}\text{Cr}$  ratios lower than 0.0009 (Table 4 and Fig. 2), which is evidenced by the similar  $\epsilon^{54}\text{Cr}$  values among the doped samples with  $^{56}\text{Fe}/^{52}\text{Cr} = 0.0002$  ( $\epsilon^{54}\text{Cr} = -0.01 \pm 0.10$ ),  $^{56}\text{Fe}/^{52}\text{Cr} = 0.0009$  ( $\epsilon^{54}\text{Cr} = 0.01 \pm 0.11$ ), and pure NIST 3112a ( $\epsilon^{54}\text{Cr} = 0.04 \pm 0.06$ ; 2SD,  $N = 4$ ) (Table 5). As for the routine measurements,  $^{56}\text{Fe}/^{52}\text{Cr}$  ratios are usually less than  $5 \times 10^{-4}$ .

**Fig. 2** Measured Cr isotope ratios for the mixture of NIST3112a and GSB Fe with different Fe/Cr ratios (0.01 ~ 1). a): the  $\epsilon^{53}\text{Cr}$  and  $\epsilon^{54}\text{Cr}$  for the mixture of NIST SRM 3112a and GSB Fe with different doped Fe/Cr ratios (0.01 ~ 1). b): the  $\epsilon^{54}\text{Cr}$  vs.  $^{56}\text{Fe}/^{52}\text{Cr}$  (measured ratios by TIMS) for the mixture of NIST SRM 3112a and GSB Fe. The error bar of  $\epsilon^{53}\text{Cr}$  and  $\epsilon^{54}\text{Cr}$  is 2SE, which are not higher than 0.06 and 0.12, respectively (Table 4).

(eluting Cr) of 3 ml 6M HCl through third column (also the third step in this study) with 0.33 ml cation resin. Zhu *et al.*<sup>13</sup> used a smaller column with only 0.1 ml of cation resin in the column. Since the resin is less, the volume of the wash acid (6M HCl) also decreases to 1 ml. Hence, using 3.3 times less resin and 3 times less acid results in  $\sim 10$  times ( $3.3 \times 3$ ) less organics introduced to the final purified Cr. Note that, the 0.1 ml column will only allow maximum  $\sim 5$  mg silicate samples were loaded and purified, relative to  $\sim 10$  mg with column of 0.33 ml resin. It will be useful to use the tiny columns to process small but Cr-rich samples, e.g., the chondrules.<sup>10</sup> Less resin and acid also introduces less Cr blanks.

**Evaluation of concentration effect.** We also did evaluation of concentration effects is to test 1) if samples and standards measured at different signals, whether it causes inaccurate data; 2) whether more loading samples and higher signals result in more precise data. Usually, 15 ~ 20 ng Cr of geological reference materials and meteorites were loaded on the Re filament in this study (Table 5). We have also tested the effect of loading a range of different Cr masses on filaments with 7.5 ng (with pilot signal

**Table 5.** The  $\epsilon^{53}\text{Cr}$  and  $\epsilon^{54}\text{Cr}$  of terrestrial geological reference materials and meteorites standards in this study

Sample Name	Cr ( $\mu\text{g/g}$ )	Type	$\epsilon^{53}\text{Cr}$	2SD	2SE	$\epsilon^{54}\text{Cr}$	2SD	2SE	N
<b>Isotope Standard</b>									
NIST 3112a + matrix* <sup>1</sup>			0.04	0.15	0.05	0.05	0.42	0.14	9
NIST 3112a* <sup>2</sup>			0.04	0.17	0.05	0.07	0.32	0.14	5
NIST 3112a (7.5 ng loading)			-0.01	0.14	0.05	0.05	0.27	0.13	11
NIST 3112a (50 ng loading)			0.09	0.14	0.04	0.00	0.34	0.10	10
<b>Terrestrial Standard</b>									
DTS-2b			-0.01	0.14	0.04	-0.04	0.39	0.12	10
DTS-2b			0.04	0.25	0.06	0.05	0.44	0.11	15
DTS-2b	15500	dunite	0.05	0.15	0.05	0.03	0.41	0.13	10
DTS-2b			0.04	0.19	0.06	0.02	0.36	0.11	10
DTS-2b			0.00	0.18	0.06	0.03	0.26	0.08	10
Mean			0.02	0.05		0.02	0.07		5
BHVO-2	287	basalt	0.01	0.09	0.02	0.04	0.29	0.08	15
BHVO-2			0.06	0.12	0.06	0.10	0.27	0.12	5
BCR-2	16	basalt	0.05	0.11	0.05	0.01	0.20	0.09	5
JP-1	2807	peridotite	0.03	0.11	0.03	0.07	0.37	0.09	15
<b>Meteorite Standard</b>									
Murchison			0.23	0.12	0.05	1.10	0.16	0.07	5
Murchison	2952	CM2 chondrite	0.27	0.13	0.04	1.12	0.35	0.12	9
Murchison			0.25	0.16	0.07	1.23	0.37	0.17	5
Mean			0.25	0.04		1.15	0.14		3
NWA 7734			0.22	0.09	0.03	-0.35	0.29	0.09	10
NWA 7734			0.24	0.15	0.04	-0.30	0.28	0.07	14
NWA 7734	n.d.	LL chondrite	0.19	0.19	0.06	-0.36	0.29	0.08	10
NWA 7734			0.23	0.11	0.04	-0.30	0.26	0.09	8
NWA 7734			0.22	0.20	0.06	-0.30	0.33	0.10	10
Mean			0.22	0.04		-0.32	0.06		5

**Notes:** \*1: The pure solution standard of NIST 3112a was analyzed after the column chemistry with the mixture of 5  $\mu\text{g}$  of pure NIST 3112a and matrix (50  $\mu\text{g}$  of Fe + Mn + Ca + Al (1:10) and 5  $\mu\text{g}$  of Ti + V + Mn + Ni + Na + K (1:1)). These matrix elements were from ultrapure GSB standards of the China Iron and Steel Research Institute. \*2: The pure solution standard of NIST 3112a was analyzed after the column chemistry. All the data are measured from different sessions.

of 7 V for  $^{52}\text{Cr}$ , 15 ng (with pilot signal of 10 V for  $^{52}\text{Cr}$ ) and 50 ng (with pilot signal of 30 V for  $^{52}\text{Cr}$ ) loads of NIST 3112a being tested (Table 5 and Fig. 3). Note that, all individual filaments have to 800 to 1800 cycles of measurement, and the data are all relative to 15 ng loading of NIST 3112a. The uncertainty for both  $\epsilon^{53}\text{Cr}$  and  $\epsilon^{54}\text{Cr}$  values do not vary with the mass of Cr loaded and the pilot signal set for the TE measurement, so high signal measurements cannot improve the data precision. By comparison, using 7.5 ng Cr loads and setting a lower TE voltage is not detrimental to precision, so for some samples, total 100 ng Cr could also be enough for a high-precision mass-independent Cr isotope measurements. However, as for the accuracy, the 50 ng (with pilot signal of 30V) measurements show non-zero  $\epsilon^{53}\text{Cr}$  values, indicating mismatch (more than three times) of the signals

between samples and standards will lead to inaccurate  $\epsilon^{53}\text{Cr}$  data.

**Precision and accuracy of Cr isotope data.** The Cr isotopic composition of both pure and doped NIST SRM 3112a, four terrestrial geological reference materials and three meteorites have each been analyzed between 5 and 15 times (Table 5 and Fig. 4). The external reproducibility is assessed as a pooled standard deviation across all reference material processed through column chromatography. The pooled standard deviation for  $\epsilon^{53}\text{Cr}$  and  $\epsilon^{54}\text{Cr}$  is 0.055 and 0.076, respectively (2 SD) and this reproducibility is comparable with what has previously been reported by TIMS<sup>16</sup> and high precision MC-ICP-MS data.<sup>23,24</sup> This figure encapsulates the reproducibility of multiple individually processed reference material aliquots and in the case of NWA7734

**Fig. 3** Measured Cr isotope ratios for the NIST 3112a with different loaded samples contents (7.5 ng, 15 ng, 50 ng). The Cr loading for 7.5 ng, 15 ng, 50 ng on each filament are analyzed on 7 V, 10V, and 30 V for  $^{52}\text{Cr}$  signal, respectively. The error bar of  $\epsilon^{53}\text{Cr}$  and  $\epsilon^{54}\text{Cr}$  is 2SE, which are not higher than 0.06 and 0.12, respectively (Table 5).

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**Fig. 4** The  $\epsilon^{53}\text{Cr}$  and  $\epsilon^{54}\text{Cr}$  of geological reference materials and meteorites standards measured by TE-TIMS in this study (“large red circles” is abbreviated to “LC”) and the literatures (“small grey circles” is abbreviated to “SC”).<sup>3,11,20,23,26,33,36,40,51</sup> The error bar of  $\epsilon^{53}\text{Cr}$  and  $\epsilon^{54}\text{Cr}$  is 2 SE respectively (Table 5). The gray bars are the average  $\epsilon^{53}\text{Cr}$  and  $\epsilon^{54}\text{Cr}$  values (with 2SD uncertainty) for bulk silicate Earth from Zhu *et al.*<sup>23</sup>

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**Fig. 5** The  $\epsilon^{53}\text{Cr}$  and  $\epsilon^{54}\text{Cr}$  of Allende meteorites standards measured by TE-TIMS (red diamonds) and normal TIMS (blue diamonds) method in this study. The Allende sample for both TIMS measurements are from same samples; Allende-a and Allende-b are two different dissolutions. The error bars of  $\epsilon^{53}\text{Cr}$  and  $\epsilon^{54}\text{Cr}$  are 2SE (Table 6). The grey shades are the average  $\epsilon^{53}\text{Cr}$  and  $\epsilon^{54}\text{Cr}$  values with 2SD uncertainty for of another Allende dissolution in Zhu *et al.*<sup>23</sup>, which are analyzed by Neptune Plus MC-ICP-MS.

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multiple individual digestions. The Cr isotopic data of JP-1 and BCR-2 were first reported in this study. All the terrestrial standards (DTS-2b, BHVO-2, JP-1, and BCR-2) analyzed in this study have  $\epsilon^{53}\text{Cr}$  and  $\epsilon^{54}\text{Cr}$  values consistent with that of BSE within our reported reproducibility.<sup>3,23,32,33,36</sup> For the meteorites, the mean  $\epsilon^{53}\text{Cr}$  values and  $\epsilon^{54}\text{Cr}$  values for the Murchison carbonaceous chondrite (CM2) is  $0.25 \pm 0.04$  ( $n = 3$ ; 2 SD);  $1.15 \pm 0.14$  ( $n = 3$ , 2 SD), respectively, which are consistent within the mean values ( $\epsilon^{53}\text{Cr} = 0.20 \pm 0.05$ ;  $\epsilon^{54}\text{Cr} = 0.95 \pm 0.05$ ) that have previously been published.<sup>23</sup> The  $\epsilon^{53}\text{Cr}$  values and  $\epsilon^{54}\text{Cr}$  values for the ordinary chondrite, NWA7734 were first reported in this study ( $\epsilon^{53}\text{Cr} = 0.22 \pm 0.04$ ,  $\epsilon^{54}\text{Cr} = -0.32 \pm 0.06$   $n = 5$ ; 2SD), and they are also similar to values for ordinary chondrites ( $\epsilon^{53}\text{Cr}$  ordinary chondrite =  $0.17 \pm 0.05$ ;  $\epsilon^{54}\text{Cr}$  ordinary chondrite =  $-0.38 \pm 0.09$ ) in previous studies.<sup>3,20,23,33,35</sup>

As a further test of to assess whether column chemistry fractionates mass-independent Cr isotope compositions, two NIST SRM 3112a standards that have been passed through all the columns have been measured. One (\*1 in Table 5), is the mixture of 5  $\mu\text{g}$  of pure NIST 3112a with 50  $\mu\text{g}$  of Fe, Mn, Ca and Al (1:10) and 5  $\mu\text{g}$  of Ti, V, Mn, Ni, Na and K (1:1), from GSB elemental standards. The second (2\* in Table 5) is pure NIST 3112a. Following measurements against unprocessed NIST SRM 3112a, the  $\epsilon^{53}\text{Cr}$  and  $\epsilon^{54}\text{Cr}$  values of these two standards after column chemistry are 0 within our reproducibility. The well consistent data for columned NIST 3112a suggests that our column chemistry does not shift the  $\epsilon^{53}\text{Cr}$  and  $\epsilon^{54}\text{Cr}$  values (Table 5) of samples (*e.g.*, through inducing non-kinetic mass-dependent fractionation).

**Comparison of TE method with normal method.** Table 6 and Fig. 5 show the comparison between Cr isotopes measured by



**Table 6.** The  $\epsilon^{53}\text{Cr}$  and  $\epsilon^{54}\text{Cr}$  of Allende (CV3 chondrite) using normal TIMS and TE-TIMS method

Method	$\epsilon^{53}\text{Cr}$	2SD	2SE	$\epsilon^{54}\text{Cr}$	2SD	2SE	N
<b>TE-TIMS*</b>							
Allende-a	0.09	0.11	0.04	0.84	0.40	0.14	8
Allende-b1	0.04	0.22	0.07	0.80	0.38	0.12	10
Allende-b2	0.05	0.15	0.05	0.86	0.18	0.06	9
Allende-b3	0.07	0.19	0.05	0.84	0.43	0.11	15
Allende-b4	0.05	0.08	0.03	0.81	0.19	0.07	7
Mean	0.06	0.04		0.83	0.04		5
<b>TIMS-Normal method</b>							
Allende-a	0.19	0.20	0.07	0.98	0.25	0.09	8
Allende-b1	0.11	0.16	0.05	0.90	0.25	0.08	10
Allende-b2	0.16	0.14	0.05	1.04	0.37	0.13	8
Allende-b3	0.16	0.20	0.07	1.03	0.37	0.13	8
Allende-b4	0.15	0.14	0.05	1.02	0.14	0.05	8
Mean	0.15	0.06		0.99	0.11		5

**Notes:** The TE-TIMS data\* in the table are from Zhu et al.<sup>50</sup> Same samples were measured on a same machine (Triton TIMS housed in Free University Berlin) using a normal TIMS-Cr method:  $\sim 2\ \mu\text{g}$  of Cr were loaded on one degassed filament; static mode; 100 cycles with integration time of 16s; the signal for  $^{52}\text{Cr}$  is  $\sim 20\ \text{V}$ ; a baseline measurement of 60 s was applied before each measurement. The Allende sample powder here is from  $\sim 5\ \text{g}$  rock pieces.

normal and TE-TIMS methods for same purified samples (from same columns and digestion) of Allende (a CV3 chondrite). All the measurements are performed on Triton TIMS housed at Freie Universität Berlin. The TE data have been published in Zhu *et al.*<sup>16</sup> It can be found that both the  $\epsilon^{53}\text{Cr}$  and  $\epsilon^{54}\text{Cr}$  values of normal measurements are systematically higher than the TE data. The differences for  $\epsilon^{53}\text{Cr}$  and  $\epsilon^{54}\text{Cr}$  values between two methods are  $\sim 0.09$  and  $\sim 0.16$  and the differences in the paired measurements lie on a line with a slope close to 2. We interpret this systematic difference as the non-kinetic Cr isotope fractionation between different Cr species (e.g.,  $\text{Cr}^+$ ,  $\text{CrO}$ ,  $\text{CrO}_2$  and  $\text{CrO}_3$ ) during Cr evaporation and ionization on TIMS. The details have been discussed in Zhu *et al.*<sup>23</sup> and Bourdon and Fitoussi.<sup>48</sup> However, TE mode aims to minimize this effect, because each measurement will evaporate all the Cr on one filament. The  $\epsilon^{53}\text{Cr}$  ( $0.10 \pm 0.04$ , 2SD) and  $\epsilon^{54}\text{Cr}$  ( $0.92 \pm 0.07$ , 2SD) data (Fig. 5, Grey bars) are another Allende dissolution (passed through 4 columns) measured by MC-ICP-MS. These values are slightly higher than the TE-TIMS data, which can be caused by sample heterogeneity.

## CONCLUSION

We report on a total evaporation TIMS method for mass-independent Cr isotope measurements. This novel method can 1) decrease the Cr quantity needed in the measurements, which is

significant for precious samples from sample return missions and some Cr-poor samples. We find that  $\sim 200\ \text{ng}$  of Cr is enough to achieve a high-precision measurements, with 2 SE uncertainties for  $\epsilon^{53}\text{Cr}$  and  $\epsilon^{54}\text{Cr}$  are  $\sim 0.05$  and  $\sim 0.10$  respectively; 2) minimize the TIMS instrumental mass fractionation of Cr isotopes achieving a better data accuracy. Based on literature study, we developed a three-step column chemistry to purify Cr from a various of samples, including basalts, peridotites and chondrites, which can also achieve a high yield ( $> 90\%$ ). We found  $\text{H}_2\text{O}_2$  at low temperature, i.e., on hot plate of  $40\ ^\circ\text{C}$ , can effectively remove the organics from the column resin.

## AUTHOR INFORMATION



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### Notes

The authors declare no competing financial interest.

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