High-Precision Measurement of Stable Cr Isotopes in Geological Reference Materials by a Double-Spike TIMS Method

Chun-Yang Liu (1), Li-Juan Xu (1)*, Chun-Tao Liu (1), Jia Liu (2), Li-Ping Qin (2), Zi-Da Zhang (1), Sheng-Ao Liu (1) and Shu-Guang Li (1, 2)

(1) State Key Laboratory of Geological Processes and Mineral Resources, School of Scientific Research, China University of Geosciences, Beijing, 100083, China
(2) CAS Key Laboratory of Crust-Mantle Materials and Environments, School of Earth and Space Sciences, University of Science and Technology of China, Hefei, 230026, China
*Corresponding author. e-mails: xulj@cugb.edu.cn and liuj08@mail.ustc.edu.cn

Chromium (Cr) isotopes have been widely used in various fields of Earth and planetary sciences. However, high-precision measurements of Cr stable isotope ratios are still challenged by difficulties in purifying Cr and organic matter interference from resin using double-spike thermal ionisation mass spectrometry. In this study, an improved and easily operated two-column chemical separation procedure using AG50W-X12 (200–400 mesh) resin is introduced. This resin has a higher cross-linking density than AG50W-X8, and this higher density generates better separation efficiency and higher saturation. Organic matter from the resin is a common cause of inhibition of the emission of Cr during analysis by TIMS. Here, perchloric and nitric acids were utilised to eliminate organic matter interference. The Cr isotope ratios of samples with lower Cr contents could be measured precisely by TIMS. The long-term intermediate measurement precision of $\delta^{53/52}\text{Cr}_{\text{SRM 979}}$ for BHVO-2 is better than ± 0.031‰ (2σ) over one year. Replicated digestions and measurements of geological reference materials (OKUM, MUH-1, JP-1, BHVO-1, BHVO-2, AGV-2 and GSP-2) yield $\delta^{53/52}\text{Cr}_{\text{SRM 979}}$ results ranging from -0.129‰ to -0.032‰. The Cr isotope ratios of geological reference materials are consistent with the $\delta^{53/52}\text{Cr}_{\text{SRM 979}}$ values reported by previous studies, and the measurement uncertainty (± 0.031‰, 2σ) is significantly improved.

Keywords: Cr isotopes, TIMS, double spike, reference materials, high precision.

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chromium Cr(III) (Rai et al. 1989, Ellis and Bullen 2002). To date, up to ~ 6–7% variation of $\delta^{53/52}Cr_{\text{NIST} \text{ SRM 979}}$ has been found during reduction and oxidation reactions (Schauble et al. 2004, Zink et al. 2010), and a large range from -0.27‰ to 1.23‰ was also found during non-redox-dependent processes (Saad et al. 2017). Accordingly, Cr isotopes have been utilised to trace the natural attenuation of Cr(VI) in groundwater (Blowes 2002) or to constrain the redox state of modern and ancient seawater (Frei et al. 2011, Bonnard et al. 2013, Scheiderich et al. 2015, Gueguen et al. 2016). A few studies have been devoted to the inventory of the solid Earth and planetary processes at high temperature, and these studies improve our understanding of the Cr cycle (Schoenberg et al. 2008, Rudge et al. 2009, Moynier et al. 2011, Farkas et al. 2013, Li et al. 2016, Xia et al. 2017). Regarding the inventory of the solid Earth, Schoenberg et al. (2008) suggested that the $\delta^{53/52}Cr_{\text{NIST} \text{ SRM 979}}$ value of the igneous silicate Earth is -0.124 ± 0.101‰ by analysing oceanic and continental basalts, mantle xenoliths, ultramafic rocks and cumulates. Farkas et al. (2013) suggested that the $\delta^{53/52}Cr_{\text{NIST} \text{ SRM 979}}$ value of the bulk silicate Earth (BSE) is -0.079 ± 0.129‰ by analysing mantle-derived chromites. Recently, Xia et al. (2017) suggested that the $\delta^{53/52}Cr_{\text{NIST} \text{ SRM 979}}$ values of fresh fertile peridotites are -0.14 ± 0.12‰ on average and the variation of $\delta^{53/52}Cr_{\text{NIST} \text{ SRM 979}}$ values of mantle peridotites is caused by partial melting. The $\delta^{53/52}Cr_{\text{NIST} \text{ SRM 979}}$ value of BSE was given as -0.11 ± 0.11‰ by analysing komatitites (Sassi et al. 2018). For the planetary processes, Moynier et al. (2011) suggested that there could be Cr isotopic fractionation during core segregation, as the $\delta^{53/52}Cr_{\text{NIST} \text{ SRM 979}}$ values of meteorites (~-0.2‰ to ~ -0.4‰) are lighter than that of the BSE. Schiller et al. (2014) also found light $\delta^{53/52}Cr_{\text{NIST} \text{ SRM 979}}$ of meteorites (~-0.3‰). However, Bonnard et al. (2016a) found that meteorites have a BSE-like stable Cr isotopic ratio and suggested that Cr isotopes are fractionated during the magmatic process. Recently, Bonnard and Halliday (2018) suggested that equilibrium fractionation between iron liquid and sulfides or kinetic fractionation during oxidation of Cr may be responsible for Cr isotopic fractionation during fractional crystallisation of meteorite rocks.

Compared with the very large Cr isotopic fractionation at low temperatures, Cr isotopic fractionation in high-temperature environments is much smaller. Thus, small measurement uncertainties during measurement of natural samples are a prerequisite to improve the application of Cr stable isotopic fractionation in high-temperature geochemistry. High-precision Cr isotopic measurements have been obtained for samples with extremely high chromium contents such as meteorite and extra-terrestrial samples (Moynier et al. 2011, Schiller et al. 2014, Bonnard et al. 2016a, b). An improved Cr isotope ratio measurement procedure for terrestrial samples that contain less chromium content is also established in this study.

The small measurement uncertainty of stable Cr isotope ratio measurement results requires not only a high-quality chemical separation process but also appropriate methods for mass bias correction, which occurs during measurement and chemical purification. High-quality Cr purification enables a reduction in the isobaric interference from $^{54}$Fe, $^{54}$V and $^{54}$Ti, and matrix element effects that interfere with the production of Cr$^+$ thermal ions (Ball and Bassett 2000). Chromium mainly has two valence states in solution, and the behaviours of Cr(III) and Cr(VI) during ion exchange separation are very different (Schoenberg et al. 2008, Trinquier et al. 2008, Yamakawa et al. 2009, Li et al. 2016, 2017). To convert all chromium ions to the same valence state, various oxidising or reducing agents ((NH$_4$)$_2$S$_2$O$_8$, K$_2$S$_2$O$_8$, KMnO$_4$, and HCl) were used in previous studies in the anion or cation resin stage, and correspondingly, two, three or even four columns were used (Table 2; Lugmair and Shukolyukov 1998, Ball and Bassett 2000, Ellis and Bullen 2002, Johnson and Bullen 2004, Halicz et al. 2008, Trinquier et al. 2008, Schoenberg et al. 2008, Yamakawa et al. 2009, Dassing et al. 2011, Schiller et al. 2014, Roell et al. 2015, Li et al. 2016, Schoenberg et al. 2016, Li et al. 2017, Zhu et al. 2018). These methods can obtain satisfactory pure Cr cuts from multiple kinds of samples. Generally, 0.5–1 µg of Cr must be loaded onto the filament for precise measurement results with the TIMS. Thus, the chemical purification process must be guaranteed to be applicable for larger test portions sizes. The residual of the oxidising reagents (SO$_4^{2-}$) can severely inhibit the Cr$^+$ signal during TIMS measurements, but this residual is difficult to remove (Ball and Bassett 2000). In addition, the high ionisation potential of Cr and the inhibition effect of the Cr$^+$ signal from organic matter during instrument measurements are the main reasons impeding the acquisition of high-precision isotope ratio results in compositionally complex geological materials during TIMS measurements (Johnson and Bullen 2004, Yamakawa et al. 2009, Chrsatny et al. 2013, Li et al. 2016).

Previous studies achieved Cr purification from meteorite and terrestrial samples by a two-step column method with AGW50-X8 (Birck and Allegré 1988, Lugmair and Shukolyukov 1998, Trinquier et al. 2008, Qin et al. 2010a, Bonnard et al. 2016b). Bonnard et al. (2011) also obtained the precise Cr isotope ratio of carbonates based on a one-step method, which has the same Cr speciation and resin types. In this study, we report an improved two-step column purification scheme without additional oxidising/reducing agent for high-precision measurement of stable Cr isotope.
Sample powders containing 0.5–1 μg Cr were digested in a combination of concentrated HF (29 mol l⁻¹) and HNO₃ (14 mol l⁻¹, 2:1 by volume) in Teflon™ PFA beakers at 130 °C for two or three days until solid particles had disappeared. Next, the solutions were heated to evaporation. Then, aqua regia (HCl: HNO₃ = 3:1) was added until the steamed sample completely dissolved. The sample solutions were evaporated to dryness on a hot plate at a surface temperature of ~130 °C. The products were finally dissolved in 0.5 ml of concentrated HCl (11 mol l⁻¹). The dissolved sample solutions were mixed with 0.4 ml SO₄²⁻–SO₄²⁻ double-spike solution for every 1 μg Cr, and then, the mixtures were heated on a hot plate at 130 °C overnight to achieve homogenisation. After evaporation to dryness, the mixtures were re-dissolved in 0.2 ml 6 mol l⁻¹ HCl.

Column chemistry

A modified method for Cr purification was developed by a two-step column procedure (Figure 1b, c, Table 1). In previous studies, cation and anion exchange resins (100–200 mesh/ 200–400 mesh) were usually used in the Cr column separation procedure (Table 2; Lugmair and Shukolyukov 1998, Ball and Bassett 2000, Ellis and Bullen 2002, Johnson and Bullen 2004, Halicz et al. 2008, Trinquier et al. 2008, Schoenberg et al. 2008, Yamakawa et al. 2009, Dassing et al. 2011, Schiller et al. 2014, Rodiller et al. 2015, Li et al. 2016, 2017, Schoenberg et al. 2016). AG50W-X8 was applied as a conventional cation exchange resin during Cr purification (Table 2, Trinquier et al. 2008, Qin et al. 2010a, Bonnand et al. 2011, 2016a, b). The purification methods applicable to silicate and meteorite materials have a limit on the minimum Cr mass fraction of the samples, and this limit is greater than approximately 45 μg g⁻¹ (Table 2). Additionally, a yield of more than 0.5 μg Cr is normally required after separation for high-precision measurement results by MS. Here, analytical grade Bio-Rad AG50W-X12 (200–400 mesh) cation exchange resins were used, and these resins have higher cross-linkage (12%), smaller wet bead size (53–106 μm) and smaller molecular weight limits (~ 400) than the Bio-Rad AG50W-X8 (200–400 mesh; cross-linkage: 8%; wet bead size: 63–150 μm; molecular weight limit: ~ 1000) cation exchange resins (http://www.bio-rad.com/en-hk/category/ ion-exchange-resins/). Thus, the AG50W-X12 (200–400 mesh) resin has a high sample load capacity so that this scheme is suitable for geological samples with variable Cr content. Silicate samples with Cr mass fractions greater than 17 μg g⁻¹ are suitable for our column chemistry, which means the maximum mass for sample powders is about 50 mg. The yield of this method is as good as published purification schemes (Table 2). The adoption of the AG50W-X12 resin also improves the separation efficiency and selectivity, which result in better separation efficiency than the Bio-Rad AG50W-X8 resin (Figure 1a, b). The retardation of Ti and V ions avoids the overlap of the elution of Cr ions and isobaric interference cations (Figure 1a, b). A better purification effect for Cr is also obtained from matrix cations such as Mg²⁺ and Ca²⁺ (Figure 1a, b).

In detail, 1 ml and 0.33 ml of Bio-Rad AG50W-X12 (200–400 mesh) cation exchange resins were loaded in columns (4 mm in diameter) with different lengths named column 1 and 2, respectively. For column 1 (Figure 1b, Table 1), the resin was washed with 5 ml 6 mol l⁻¹ HCl and 3 ml HPW, and was pre-conditioned with 5 ml 1 mol l⁻¹ HCl. Prior to launching the Cr column, the samples were diluted with HPW to a total volume of 1.2 ml 1 mol l⁻¹ HCl solution and then loaded carefully onto the resin beds. Chromium in the samples formed as Cr(III)-Cl complexes in concentrated HCl at 130 °C and was further eluted with 3.5 ml 1 mol l⁻¹ HCl (Larsen et al. 2016). Then, sub-purified
Cr samples were re-digested with 20 μl concentrated HNO₃ and diluted with 2 ml HPW (~0.16 mol l⁻¹ HNO₃) before loading on column 2. The Fe, V and matrix elements were almost completely removed by column 1 (Figure 1b, Table 1). For column 2 (Figure 1c, Table 1), the resin was washed with 4 ml 6 mol l⁻¹ HCl and 3 ml HPW. The chromium aliquots from column 1 were loaded onto column 2, which was pre-conditioned with 5 ml 0.16 mol l⁻¹ HNO₃. After sample loading, Ti and Al ions were removed by 3 ml 0.5 mol l⁻¹ HF, and V and other matrix elements were eluted again by following 10 ml 1 mol l⁻¹ HCl. Chromium was eluted with 4 ml 2 mol l⁻¹ HCl. After column separation, the final Cr cuts were dried down in concentrated HNO₃ (14 mol l⁻¹) several times and then dissolved with concentrated HNO₃ and HClO₄ acid to eliminate organic matter before isotopic measurement.

By implementing a two-step separation procedure, we obtained a highly purified Cr fraction (Figure 1b, c). The Cr yields after the two-column chemistry were higher than 85%, and the whole-procedure Cr blank was less than 3–4 ng, which was considered to be negligible (lower than 0.5%) relative to total amount of loaded Cr (1000 ng). The Cr yields were tested using BHVO-2 by ICP-MS, and the whole-procedure Cr blank was also measured by ICP-MS.

**Cr double-spike technique**

The $^{50}$Cr,$^{54}$Cr double spike is usually used to correct the mass dependence fractionation generated during sample processing as well as by instrumental mass bias effects for the Cr isotope ratio of samples (Ellis and Bullen 2002, Schoenberg et al. 2008, Frei et al. 2009, Zink et al. 2010, Qin et al. 2010a, Bonnard et al. 2011, Farkas et al. 2013, Planavsky et al. 2014, Wang et al. 2016, Cole et al. 2016, Li...
each analysis, temperature of the collectors (298 K) and ion beam voltage of each isotope, integration time, cycles of by MATLAB, and the results are presented in Figure 2a. The simulation was implemented to eliminate all gain calibration errors. The total acquisition time was approximately 60 min for one filament, including a 60 s baseline measurement at the beginning and after every seven blocks of data acquisition. Each block included a 60 s baseline measurement and seven blocks of data acquisition. Amplifier gains were calibrated at the start of each day and the remaining organics were removed by a brief heating procedure. Then, a mixture solution of 1.3 μl high purity (99.99%) silica gel (< 100 nm) and 1.3 μl saturated H₂BO₃ was added to the sample drops. The mixture was first dried by slow heating under low current conditions (~0.5 A) through the filament to form a glass, and then, the current was increased slowly until the filament was dull red (~2.2 A) for 2 s. Every filament load standard or sample contained 0.5–1 μg of Cr. One sample was loaded on 1–2 filaments. All Cr isotopic data were acquired in static multi-collection mode by the collector array summarised in Table 3. Ion beam measurements at m/z 49(Ti⁺), 51(V⁺) and 56(Fe⁺) allowed us to correct isobaric interferences from Ti⁺ and V⁺ on Cr⁺ and Fe⁺ on Cr. During a measurement routine, the filament was heated to 1500 mA in 5 min and then heated to 1800 mA in 3 min. Generally, data acquisition started when the current beam of 53(Cr⁺) was stable and higher than 4 × 10⁻¹¹ A and the temperature of the filaments was ca. 1330 °C. For each analysis, fourteen blocks of twelve cycles at integration times of 8 s were obtained using amplifier rotation. Each block included a 60 s baseline measurement. Amplifier gains were calibrated at the start of each day to eliminate all gain calibration errors. The total acquisition time was approximately 60 min for one filament, including a 15 min heating routine. Each filament was monitored three or four times.

Table 1. Chromium chemistry purification procedure and the function of each step

| Separation stage | Reagent | Volume (ml) |
|------------------|---------|-------------|
| **Column 1: Cation exchange resin (AG50W-X12, 200-400 mesh, 1 ml)** | | |
| Condition | 1 mol ¹¹HCl | 5 |
| Load sample and collect Cr | 1 mol ¹¹HCl | 1.2 |
| Collect Cr | 1 mol ¹¹HCl | 1 |
| Collect Cr | 1 mol ¹¹HCl | 2.5 |
| Elute Fe, V and matrix | 6 mol ¹¹HCl | 7 |
| **Column 2: Cation exchange resin (AG50W-X12, 200-400 mesh, 0.33 ml)** | | |
| Condition | 0.16 mol ¹⁷HNO₃ | 4 |
| Load sample | 0.16 mol ¹⁷HNO₃ | 2 |
| Elute Ti and V | 0.5 mol ¹¹HF | 3 |
| Elute Mn and matrix | 1 mol ¹¹HCl | 1 |
| Elute Mn and matrix | 1 mol ¹¹HCl | 3 |
| Elute Mn and matrix | 1 mol ¹¹HCl | 3 |
| Elute Mn and matrix | 1 mol ¹¹HCl | 3 |
| Collect Cr | 2 mol ¹¹HCl | 2 |

The Monte Carlo method was used to predict optimised the spike/ (spike + sample) ratios (Q) and ratios of double spike (P). Lehner et al. (2013) further proposed an improved method to simulate TIMS analysis by considering Faraday collector damage and achieved excellent repeatability precision of ~ 0.024‰ (2 SE) for Ca isotope ratio measurement results. Here, according to the mathematical equations presented by Lehner et al. (2013), the Monte Carlo simulation, mainly, takes counting statistics (σₙ) and Johnson noise (σₙ) into consideration to optimise spike/ (spike + sample) ratios (Q) and the ratios of ⁵⁰Cr spike and ⁵⁴Cr spike (P) of Cr isotopes (Figure 2a). The simulation was implemented by MATLAB, and the results are presented in Figure 2a. The ion beam voltage of each isotope, integration time, cycles of each analysis, temperature of the collectors (298 K) and amplifier resistance are all involved in calculation of the theoretical uncertainty curve, which was consistent with that in the experiment. We mixed two single spikes as a ⁵⁴Cr/ ₉₇₉ total of 0.484. The ⁵⁴/⁵₂Cr of NIST SRM 979 mixed with different double-spike proportions was determined by TIMS, and the experimental error matched the theoretical simulation uncertainty curve of ⁵⁴/⁵₂Cr of NIST SRM 979 (Figure 2b, Table S1). Given that the ratio of ⁵⁴Cr/ ₉₇₉ total in double spike is 0.484, the optimal spike proportion should be 10% to 40% of the total Cr (Crspike + Crsample); hence, we selected a Crspike/Crtotal ratio of 0.25 in our method.

**Mass spectrometric measurements**

The measurements of Cr isotope ratios were performed on a Thermo Fisher Scientific TRITON Plus TIMS in the Isotope Geochemistry Lab of the China University of Geosciences, Beijing. This instrument was equipped with nine Faraday cups linked to 10⁻¹¹ Ω amplifiers. Chromium was loaded in 2 μl of 3% m/v HNO₃ onto outgassed Re single filaments under a binocular microscope using a 0.5–10 μl digital pipette. Narrow paraffin dams were placed on the filaments to facilitate the core formation of sample aliquots, and the remaining organics were removed by a brief heating procedure. Then, a mixture solution of 1.3 μl high purity (99.99%) silica gel (< 100 nm) and 1.3 μl saturated H₂BO₃ was added to the sample drops. The mixture was first dried by slow heating under low current conditions (~0.5 A) through the filament to form a glass, and then, the current was increased slowly until the filament was dull red (~2.2 A) for 2 s. Every filament load standard or sample contained 0.5–1 μg of Cr. One sample was loaded on 1–2 filaments. All Cr isotopic data were acquired in static multi-collection mode by the collector array summarised in Table 3. Ion beam measurements at m/z ⁴⁹(Ti⁺), ⁵¹(V⁺) and ⁵⁶(Fe⁺) allowed us to correct isobaric interferences from Ti⁺ and V⁺ on Cr⁺ and Fe⁺ on Cr. During a measurement routine, the filament was heated to 1500 mA in 5 min and then heated to 1800 mA in 3 min. Generally, data acquisition started when the current beam of ⁵³(Cr⁺) was stable and higher than 4 × 10⁻¹¹ A and the temperature of the filaments was ca. 1330 °C. For each analysis, fourteen blocks of twelve cycles at integration times of 8 s were obtained using amplifier rotation. Peak centre and auto-focus were applied at the beginning and after every seven blocks of data acquisition. Each block included a 60 s baseline measurement. Amplifier gains were calibrated at the start of each day to eliminate all gain calibration errors. The total acquisition time was approximately 60 min for one filament, including a 15 min heating routine. Each filament was monitored three or four times.

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The $^{53}\text{Cr}/^{52}\text{Cr}$ ratios of the samples are expressed as the per mil deviation from the Cr isotope reference material NIST SRM 979 measured in the same barrel:

$$
\delta^{53/52}\text{Cr}_{\text{NIST SRM 979}} = \frac{R(\text{NIST SRM 979})}{R(\text{Sample})} \times 10^3 \text{ (1)}
$$

### Results and discussion

#### Evaluation of Ti, V and Fe isobaric interference and other matrix interference

Iron is a major element, and Ti and V are trace elements in geological materials. All of these elements have direct

### Table 2.
Reported methods for Cr separation

| Reference           | Ion exchanger               | Sample type                  | Lowest Cr mass fraction ($\mu$g g$^{-1}$) | Cr yield after separation ($\mu$g) | Yield (%) |
|---------------------|-----------------------------|------------------------------|------------------------------------------|-----------------------------------|-----------|
| This study          | AG50W-X12 (200–400 mesh)    | Silicate                     | 17                                       | 1                                 | 85        |
|                     | AG50W-X12 (200–400 mesh)    | BIF                          | 0.5                                      | 2.5                               | 80-90     |
|                     | AG1-X8                      | Chondrite and silicate       | 45.4                                     | 4-20                              | n.d.      |
|                     | AG50W-X8 (200-400 mesh)     | Basalt, shale, ultramafic rocks and cumulates | 42.51 | n.d. | 70-85 |
|                     | AG50W-X8 (200-400 mesh)     | Terrestrial rock and chondrite | 280 | 1-2 | 80 |
|                     | AG50W-X8 (200-400 mesh)     | More basalts                 | 1410                                      | 1                                 | 80        |
|                     | AG50W-X8 (200-400 mesh)     | Carbonate and silicate       | 5                                         | > 0.05                            | 94.7-97.5 |
|                     | AG1-X8 (200-400 mesh)       | Seawater                     | n.d.                                      | 0.08-0.3                          | n.d.      |
|                     | AG50W-X8 (200-400 mesh)     | Meteorites                   | n.d.                                      | n.d.                              | 80        |
|                     | AG50W-X8 (200-400 mesh)     | Carbonates                   | 0.19                                      | 0.5-6                             | n.d.      |
|                     | AG50W-X8 (200-400 mesh)     | Carbonates                   | 1.05                                      | 0.25                              | 70-80     |
|                     | AG50W-X8 (200-400 mesh)     | Marine sediments             | 17                                       | n.d.                              | 75-85     |
|                     | AG50W-X8 (200-400 mesh)     | Silicate                     | n.d.                                      | 0.5-3                             | n.d.      |
|                     | AG50W-X8 (200-400 mesh)     | Cr(VI) stock solution        | 0.08                                      | 43230                             | > 95      |
|                     | AG50W-X8                   | Water                        | n.d.                                      | 0.665                             | 90        |
|                     | AG1-X8                     | Chromites, ultramafic rocks  | 976                                       | 2                                 | 90-95     |
|                     | AG 1-X8                    | n.d.                         | 0.25                                      | n.d.                              | n.d.      |
|                     | AG1-X8                     | Silicate                     | 320                                       | n.d.                              | > 95      |
|                     | AG50W-X12                  | Dunite, meteorites           | n.d.                                      | 3-6                               | n.d.      |
|                     | AG1-X8                     | Carbonate, silicate, shale, soil, plants and animals | 0.41 | 0.3-0.6 | 80-98 |
|                     | AG50W-X8                   |                              |                                           |                                   |           |
|                     | AG1-X8                     |                              |                                           |                                   |           |
|                     | AG1-X8                     |                              |                                           |                                   |           |
|                     | AG1-X8                     |                              |                                           |                                   |           |
|                     | AG1-X8                     |                              |                                           |                                   |           |
|                     | AG1-X8                     |                              |                                           |                                   |           |

n.d.: no data were reported.
isobaric interference on the ion beam of Cr isotopes. In addition, matrix elements (K, Na, Ca and Mg) suppress the emission of Cr on the filament, and this suppression may affect the uncertainty of measurement results of Cr isotopes. Hence, it is important to evaluate the potential effects of isobaric interference from Ti, V, Fe and other matrix elements, even though our Cr separation method provides good separation of Cr from terrestrial samples. To evaluate the isobaric interferences from Ti, V and Fe, 1 μg of unspiked GSB-Cr calibrator was doped with different amounts of GSB-Ti, V and Fe calibration standard solutions (Figure 3, Table S2). The isobaric elements/Cr concentration ratios ranged from 0.001 to 10. We also doped a mixture of K, Na, Ca and Mg to evaluate the inhibition effects from these matrix elements on the Cr⁺ signal intensity during determination (the ratio of mixture to Cr ranged from 0.01 to 0.1). As a result of high ionisation potential, Ti and V are very difficult to ionise with TIMS – a finding also proposed by Li et al. (2016) (Figure 2). Nevertheless, we could not obtain a stable Cr⁺ single when the ratio of Ti to Cr is greater than 0.01. The presence of Ti suppresses the signal intensity of Cr⁺ and results in poor precision (Li et al. 2016). We also noticed that the signal of Cr⁺ attenuates rapidly during determination. No signals of 51(V⁺) and 49(Ti⁺) were detected during instrument measurements, as the 49Ti/52Cr and 51V/52Cr ratios of samples doped with GSB-Ti and V were indistinguishable from those of the pure GSB-Cr calibration material. This finding suggests that Ti and V only inhibit the emission of Cr but show no isobaric interferences. The mixture of K, Na, Ca and Mg provides a similar effect as that of Ti and V for Cr isotope measurement (Figure 3). However, the presence of both Cr⁺ and Fe⁺ beams can be observed in pure GSB-Cr doped with Fe during measurement, and a weak positive relationship was observed between the 53Cr/52Cr ratios and the amount of

Table 3.
Cup configuration for Cr isotope measurement

| Element | L4 | L2 | L1 | C | H1 | H2 | H3 |
|---------|----|----|----|---|----|----|----|
| Cr      | 49Ti | 50Cr | 51V | 52Cr | 53Cr | 54Cr | 56Fe |

Figure 2. (a) 3D contour plot of doubling the standard error (2 SE), as a function of proportion of 50Cr spike in the double spike and spike/sample ratios. The horizontal axis gives the proportion Q of double spike in the double spike–sample mixture, and the vertical axis gives the proportion P of 54Cr in the double spike. (b) Comparison between theoretically simulated and measured error under the 54Cr spike proportion is 0.484. The theoretical doubling the standard error of δ53Cr was calculated by the double-spike equation described in Lehn et al. (2013). Noted that there is a broad region around the optimum ratios. [Colour figure can be viewed at wileyonlinelibrary.com]
added Fe (Figure 3). The samples doped with less than 1 μg Fe could show bias-free $^{53}$Cr/$^{52}$Cr ratios depending on our analysis (Figure 3). Iron can be ionised with Cr due to the lower ionisation potential than Ti and V at slightly higher temperature. Excess Fe caused strong $^{56}$(Fe$^+$) signal interference and inhibited the emission of Cr$^+$ for a sample doped with 10 μg Fe (Figure 3). It is noteworthy that the current beam of $^{56}$(Fe$^+$) increases with temperature, especially when the temperature is higher than 1350 °C. Therefore, in our experience, data acquisition should be treated carefully when the temperature of the filaments reaches 1350 °C.

In contrast to analysis by MC-ICP-MS, Cr isotopic measurements by TIMS do not have strong isobaric and matrix interferences, as the Ti, V and most of the Fe have low ionisation efficiency or even no ionisation due to the high ionisation potential and different ionisation temperature relative to those of the Cr isotope (Li et al. 2016). The addition of Ti, V and Fe inhibits the ionisation of Cr, and only Fe can be ionised with Cr (Figure 3).

**Elimination of organic matter in the sample after chemical separation**

During the measurement of Fe, Cr, Pb and Cu isotopes using TIMS, organic matter is considered a significant interference (Kuritani and Nakamura 2002, Johnson and Bullen 2004, Yamakawa et al. 2009, Chrustny et al. 2013).

The organic matter in samples is most likely derived from the exchange resin or colloidal silica. Previous work used ultraviolet radiation, H$_2$O$_2$ or HClO$_4$ treatment to eliminate organic residues originating from the column resin (Kuritani and Nakamura 2002, Johnson and Bullen 2004, Yamakawa et al. 2009, Chrustny et al. 2013). During our experiment, the beam current of $^{52}$(Cr$^+$) increased smoothly and was stable over 10 x 10$^{-11}$ A when 0.5 μg of pure Cr isotope reference materials NIST SRM 979 and NIST SRM...
3112a were measured. By contrast, the beam of $^{52}\text{Cr}^+$ in NIST SRM 979, NIST SRM 3112a or geological reference materials (~ 0.5–1 µg Cr) that underwent chemical procedures usually did not exceed 1 or $2 \times 10^{-11}$ A and attenuated to zero rapidly. Thus, the elimination of organic matter is required for the measurement of high-precision Cr isotope ratio in complex rock samples.

The organic component in samples is highly persistent after the repeated drying of samples with drops of nitric acid at elevated temperature or adding $\text{H}_2\text{O}_2$ (Kuritani and Nakamura 2002, Johnson and Bullen 2004, Yamakawa et al. 2009, Chrañny et al. 2013). Both $\text{H}_2\text{O}_2$ and $\text{HNO}_3$ were tried many times to eliminate organic matter after Cr purification with different temperature/time conditions (for the repeated digestion of a BHVO-2 sample with 1 µg Cr). As shown in Figure 4, the signal intensity decayed rapidly after drying 4–8 times repeatedly samples with drops of $\text{H}_2\text{O}_2$ and similar results were obtained even at room temperature/ heating the samples with $\text{H}_2\text{O}_2$ at 70 °C for 1–14 days. The signal intensity also decayed after repeatedly drying samples 5–8 times with drops of $\text{HNO}_3$.

$\text{HClO}_4$ has not been commonly used recently, as perchloric acid results in Cr loss by evaporation of Cr (Makishima et al. 2002). However, in this study, an optimised process performed with $\text{HClO}_4$, which is the most effective medium to eliminate organic interference after trying different processes ($\text{HNO}_3$/ $\text{H}_2\text{O}_2$ with different temperature/time conditions). All samples were heated on a 120 °C hot plate with 500 µl concentrated $\text{HNO}_3$ and 30 µl $\text{HClO}_4$ for two weeks to obtain a high and stable beam intensity of $^{52}\text{Cr}^+$ (Figure 4, Table S3). The reaction rate did not clearly increase with increasing temperature but was coupled with the reaction time. Attempts to shorten the sample processing time at 120 °C or higher did not yield the satisfactory effect of eliminating organic interference. In addition, the degree of elimination of the organic matter with pure $\text{HClO}_4$ is limited without the cooperative effect of $\text{HNO}_3$. The procedural blank from $\text{HClO}_4$ was negligible, as the $\text{HClO}_4$ was purified. As shown in Figure 5b, $\delta^{53/52}\text{Cr}_{\text{NIST SRM 979}}$ values at every point were obtained during repeated measurements of one sample on one loaded filament with repeated sample digestion. High-precision Cr isotope measurement results, with a typical high and stable beam of $^{52}\text{Cr}^+$ (> 4 $\times$ 10$^{-11}$ A), were achieved for every repeated geological sample after elimination of the organic component by $\text{HNO}_3$ and $\text{HClO}_4$ (Figure 5b). The long-term intermediate precision for both USGS BHVO-2 and JP-1 was less than 0.035‰ for measurements over two years (Figure 5b). As suggested by Makishima et al. (2002), the addition of perchloric acid results in Cr loss by evaporation.

![Graphs](image-url)
of Cr in the form of CrO₂Cl₂ in the process of drying (Makishima et al. 2002, Li et al. 2017). The boiling point temperature of CrO₂Cl₂ is 116.85 °C (390 K). In this study, because of the low boiling temperature of concentrated HNO₃ (83 °C), HClO₄ can evaporate the solution to dryness with HNO₃ at only 105 °C to avoid the loss of Cr.

Geological reference materials such as BHVO-1, BHVO-2, and JP-1 all produced a stable (Figure 5b) and high beam intensity of ⁵²⁵²Cr⁻ (i.e., 4–12 V) after eliminating organic matter. One measurement result for BHVO-1 was slightly higher than the mean value of BHVO-1 in our laboratory, as the repeated measurements on the filament resulted in an excessive filament temperature (1380 °C). The ⁵⁴Fe/⁵²Cr ion beam ratio of this BHVO-1 sample (2.74 × 10⁻⁴) is two orders of magnitude higher than that of the pure Cr isotope reference material, and these data are consistent with mean value of δ⁵³/⁵²CrNIST SRM 979 of BHVO-1 in our laboratory within the given precision. Nevertheless, a small mass of Fe is ionised at this temperature, perhaps resulting of a shift of the δ⁵³/⁵²CrNIST SRM 979 of BHVO-1. This observation is consistent with our previous discussion. To achieve high-precision Cr isotope determination, a steady filament temperature should be maintained at approximately 1350 °C during measurement.

Performance of the new measurement procedure

Our long-term instrumental stability was established by measuring the spiked NIST SRM 979 Cr reference material and NIST SRM 3112a Cr reference material over a period of sixteen months (Figure 6). The δ⁵³/⁵²CrNIST SRM 979 values were determined by the double-spike technique and normalised by the daily mean of the δ⁵³/⁵²CrNIST SRM 979 value of the isotopic reference material NIST SRM 979 to eliminate the small offset from the instrument’s mass bias and double-spike technique. The δ⁵³/⁵²CrNIST SRM 979 value of NIST SRM 979 was 0.000 ± 0.017‰ (2σ, n = 163) and that of δ⁵³/⁵²CrNIST SRM 979 of NIST SRM 3112a was -0.069 ± 0.025‰ (2σ, n = 169) relative to that of NIST SRM 979. Our NIST SRM 3112a δ⁵³/⁵²CrNIST SRM 979 value is in excellent agreement with previous studies (i.e., -0.067 ± 0.024‰, Schoenberg et al. 2008, -0.09 ± 0.04‰, Xia et al. 2017, -0.07 ± 0.04‰, Shen et al. 2018). To check the stability of the measurement results, we also analysed the mass-independent Cr isotope ratios (after internal normalisation using the ⁵⁰Cr/⁵²Cr ratio) of these two isotope reference materials without double-spike addition over a period of six months. The ⁵³Cr/⁵²Cr and ⁵⁴Cr/⁵²Cr ratios of NIST SRM 979 and NIST SRM 3112a were stable and uniform, with ⁵³Cr/⁵²Cr ratios of NIST SRM 979 and NIST SRM 3112a of 0.1134616 ± 0.000002 (2σ, n = 22) and 0.1134617 ± 0.000002 (2σ, n = 63) and ⁵⁴Cr/⁵²Cr ratios of NIST SRM 979 and NIST SRM 3112a of 0.028214 ± 0.000001 (2σ, n = 22) and 0.028214 ± 0.000001 (2σ, n = 63), respectively (Figure 7).

![Figure 7. Mass-independent isotopic ratios (a) ⁵³Cr/⁵²Cr and (b) ⁵⁴Cr/⁵²Cr for NIST SRM 979 and NIST SRM 3112a measured from May 2016 to September 2016. The instrumental mass fractionation of Cr was corrected by assuming a constant ratio of 0.051859 (Shields et al. 1963) for ⁵⁰Cr/⁵²Cr and an exponential mass fractionation law. (Colour figure can be viewed at wileyonlinelibrary.com)](image-url)
independent digestion and duplicate measurement results of geological reference materials.

Previous studies revealed that the Cr(II)/Cr(III) ratios of mantle melts and basaltic melts can significantly vary depending on the oxygen fugacity and the composition of the melts. Divalent chromium is likely to be the dominant species in basaltic melts (Berry et al. 2006). Recently, studies have found that partial melting of the mantle may cause a small but detectable (~ 0.4‰ of $\delta^{53/52}$CrNIST SRM 979) stable Cr isotopic fractionation (Schoenberg et al. 2016, Xia et al. 2017). The oxygen fugacity variation may dominate the mass-dependent chromium stable isotope fractionation in high-temperature processes (Bonnand and Halliday 2018, Shen et al. 2018). Thus, stable Cr isotopic fractionation may be observed between mantle and basalts, given the different Cr(II)/Cr(III) ratios of mantle melts and basaltic melts (Schoenberg et al. 2008). In this study, two basalt reference materials from the USGS, BHVO-1 (~0.120 ± 0.029‰, 2s) and BHVO-2 (~0.129 ± 0.032‰, 2s), gave slightly lower $\delta^{53/52}$CrNIST SRM 979 values than that of peridotite reference material JP-1 from JSG (~0.088 ± 0.034‰, 2s) with the mean results over a period of two years. The data obtained in this study for these basalt and peridotite reference materials are consistent with the $\delta^{53/52}$CrNIST SRM 979 values reported by previous studies within the precision quoted (Schoenberg et al. 2008, 2016, Wang et al. 2016, Li et al. 2016, 2017, Gueguen et al. 2016, Bonnand et al. 2016a, b, Wu et al. 2017, Xia et al. 2017, Zhu et al. 2018) (Figure 5b).

We also report the $\delta^{53/52}$CrNIST SRM 979 values for komatiite reference material (OKUM), ultramafic rocks reference material (MUH-1), and two intermediate and felsic igneous reference materials (AGV-2 and GSP-2). The $\delta^{53/52}$CrNIST SRM 979 values for OKUM, MUH-1, AGV-2 and GSP-2 are -0.072 ± 0.025‰ (2s), -0.032 ± 0.029‰ (2s), -0.051 ± 0.031‰ (2s) and -0.075 ± 0.049‰ (2s), respectively. Each sample was loaded onto one filament and measured twice with a beam of $^{52}$Cr over 2 × 10^-11 A. Thus, the Cr isotope ratio of geological samples with a lower chromium mass fraction (20 µg g^-1) can also be determined precisely without an inhibition effect from organic matter. Overall, seven igneous rock reference materials analysed in this study yielded $\delta^{53/52}$CrNIST SRM 979 values ranging from -0.129 ± 0.032‰ (2s) to -0.032 ± 0.029‰ (2s), which is distinguishable within our measurement uncertainty, demonstrating detectable stable Cr isotopic fractionation during high-temperature processes.

### Table 4.
Chromium isotopic composition of geological reference materials in this study and in the literature

| Sample name | Sample type | Reference | Cr (µg g^-1) | $\delta^{53/52}$CrNIST SRM 979(‰) | 2s | N |
|-------------|-------------|-----------|-------------|-----------------------------------|----|----|
| JP-1        | Peridotite  | This study| 2807        | -0.09                             | 0.034 | 21 |
|             |             | Schoenberg et al. (2016) | -0.067 | n.d. | n.d. | |
|             |             | Bonnand et al. (2016a) | -0.128 | 0.022 | 14 | |
|             |             | Bonnand et al. (2016b) | -0.102 | 0.012 | 5 | |
|             |             | Li et al. (2016) | -0.112 | n.d. | n.d. | |
|             |             | Zhu et al. (2018) | -0.05 | 0.06 | 3 | |
| BHVO-2      | Basalt      | This study| 280        | -0.13                             | 0.032 | 18 |
|             |             | Wang et al. (2016) | 0.11 | 0.08 | 7 | |
|             |             | Gueguen et al. (2016) | -0.12 | 0.09 | 25 | |
|             |             | Schoenberg et al. (2008) | -0.126 | 0.084 | 3 | |
|             |             | Wu et al. (2017) | -0.09 | 0.03 | 8 | |
|             |             | Schoenberg et al. (2016) | -0.178 | n.d. | n.d. | |
|             |             | Li et al. (2016) | -0.155 | n.d. | n.d. | |
|             |             | Li et al. (2017) | -0.165 | n.d. | n.d. | |
|             |             | Zhu et al. (2018) | -0.12 | 0.04 | 15 | |
| BHVO-1      | Basalt      | This study| 271        | -0.13                             | 0.029 | 12 |
|             |             | Schoenberg et al. (2016) | -0.178 | n.d. | n.d. | |
|             |             | Schoenberg et al. (2008) | -0.126 | 0.084 | 3 | |
|             |             | Xia et al. (2017) | -0.07 | 0.05 | 5 | |
| GSP-2       | Granodiorite| This study| 20         | -0.08                             | 0.049 | 4 | |
|             |             | Zhu et al. (2018) | -0.1 | 0.02 | 3 | |
| AGV-2       | Andesite    | This study| 17         | -0.05                             | 0.031 | 1 | |
|             |             | Zhu et al. (2018) | -0.14 | 0.04 | 4 | |
| MUH-1       | Ultramafic rock | This study | 2727    | -0.032                           | 0.029 | 3 | |
| OKUM        | Komatiite   | This study| 2385       | -0.072                           | 0.025 | 3 | |

n.d.: no data were reported
Summary

High-precision Cr isotope measurement results for natural samples were obtained with double-spike TIMS. A two-
step separation of Cr from geological materials without using additional oxidisation reagent was presented in this study. A stable and strong Cr\(^{2+}\) beam was obtained with the elimination of organic matter in the sample after the described chemistry procedure involving perchloric acid and concentrated H\(\text{NO}_3\). The measurement uncertainty in this study was assessed by multiple analyses of the NIST SRM 979 and NIST SRM 3112a reference materials. The \(\delta^{53/52}\text{Cr}_{\text{NIST SRM 979}}\) values obtained are \(0.000 \pm 0.017\‰\) (2s, \(n = 163\)) and \(-0.069 \pm 0.025\‰\) (2s, \(n = 169\)), respectively, to that of NIST SRM 979. We also reported Cr isotopic data for seven geological reference materials relative to NIST SRM 979. Basalt reference materials (\(\delta^{53/52}\text{Cr}_{\text{NIST SRM 979}}\) of BHVO-1 = \(-0.120 \pm 0.029\‰\), 2s, BHVO-2 = \(-0.129 \pm 0.032\‰\), 2s) have lower lighter \(\delta^{53/52}\text{Cr}_{\text{NIST SRM 979}}\) values than peridotite reference material (JP-1 = \(-0.088 \pm 0.034\‰\), 2s). These rock reference materials ranging in composition from ultramafic to felsic yielded \(\delta^{53/52}\text{Cr}_{\text{NIST SRM 979}}\) values ranging from \(-0.129 \pm 0.032\‰\) (2s) to \(-0.032 \pm 0.029\‰\) (2s), which are distinguishable within our measurement uncertainty.

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**Supporting information**

The following supporting information may be found in the online version of this article:

- Table S1. Raw data for NIST SRM 979 with different spike ratios.
- Table S2. Raw data for unspiked GSB-Cr doped with different proportion of Ti, V, Fe and matrix elements.
- Table S3. Raw data for samples after column chemistry with different procedures.

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