

# JAAS

Accepted Manuscript



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

*Accepted Manuscripts* are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

# Precise measurement of chromium isotopes by MC-ICPMS

Martin Schiller,<sup>\*a</sup>, Elishevah Van Kooten,<sup>a</sup> Jesper C. Holst,<sup>a</sup> Mia B. Olsen,<sup>a</sup> and Martin Bizzarro<sup>a</sup>

Received Xth XXXXXXXXXXXX 20XX, Accepted Xth XXXXXXXXXXXX 20XX

First published on the web Xth XXXXXXXXXXXX 200X

DOI: 10.1039/b000000x

We report novel analytical procedures allowing for the concurrent determination of the stable and mass-independent Cr isotopic composition of silicate material by multiple collector inductively coupled mass spectrometry (MC-ICPMS). In particular, we focus on improved precision of the measurement of the neutron-rich isotope  $^{54}\text{Cr}$ . Because nitride and oxide interferences are a major obstacle to precise and accurate  $^{54}\text{Cr}$  measurements by MC-ICPMS, our approach is designed to minimize these interferences. Based on repeat measurements of standards, we show that the mass-independent  $^{53}\text{Cr}$  and  $^{54}\text{Cr}$  compositions can be routinely determined with an external reproducibility better than 2.5 and 5.8 ppm (2 sd), respectively. This represents at least a two-fold improvement compared to previous studies. Although this approach uses significantly more Cr (30-60  $\mu\text{g}$ ) than analysis by thermal ionization mass spectrometry (TIMS), our result indicate that it is possible to obtain an external reproducibility of 19 ppm for the  $\mu^{54}\text{Cr}$  when consuming amounts similar to that typically analyzed by TIMS (1  $\mu\text{g}$ ). In addition, the amount of time required for analysis by MC-ICPMS is much shorter thereby enabling a higher sample throughput. As a result of the improved analytical precision, we identified small apparent mass-independent differences between different synthetic Cr standards and bulk silicate Earth (BSE) when using the kinetic law for mass bias correction. These differences are attributed to Cr loss by equilibrium processes during production of the synthetic standards. The stable isotope data concurrently obtained has a precision of 0.05‰/Da, which is comparable to earlier studies. Comparison of the measured isotopic composition of four meteorites with published data indicate that Cr isotope data measured by the technique described here are accurate to stated uncertainties. The stable Cr composition of the Bilanga and NWA 2999 achondrites suggest that the differences in the stable Cr isotope composition of Earth and chondrites may reflect heterogeneity of their precursor material rather than Cr isotope fractionation during metal-silicate segregation of Earth. Lastly, a step wise dissolution experiment of the CI chondrite Ivuna reveals previously unknown carriers of large mass-dependent Cr stable isotope variations that co-vary with the known presence of carriers of large nucleosynthetic anomalies, demonstrating one advantage of this technique.

## 1 Introduction

Chromium has four naturally occurring isotopes –  $^{50}\text{Cr}$ ,  $^{52}\text{Cr}$ ,  $^{53}\text{Cr}$  and  $^{54}\text{Cr}$  – with relative abundances of 4.35%, 83.79%, 9.50% and 2.36%, respectively. Variations in the relative abundances of these isotopes in meteorites and the terrestrial rock record can be used to study processes associated with the formation and evolution of the earliest solar system as well as ancient and modern terrestrial environments (e.g.,<sup>1-4</sup>). In cosmochemistry, chromium is particularly useful because the abundance of  $^{53}\text{Cr}$  and  $^{54}\text{Cr}$  provides temporal and spatial information on early solar system processes (e.g.,<sup>1,5-7</sup>). Given that the documented Cr isotope variations are typically small, improving the precision of Cr isotope measurements can potentially allow for a better understanding of the processes that shaped our solar system.

Of the two Cr isotopes particularly relevant to cosmochemists, namely  $^{53}\text{Cr}$  and  $^{54}\text{Cr}$ , the neutron-rich  $^{54}\text{Cr}$  nuclide is pre-

dominantly produced by neutron-rich statistical equilibrium or quasi-equilibrium processes occurring in a type Ia supernova<sup>8-10</sup>. In contrast,  $^{50}\text{Cr}$ ,  $^{52}\text{Cr}$ , and  $^{53}\text{Cr}$  are primarily the products of explosive oxygen and silicon burning in supernovae<sup>10</sup>. The major nucleosynthetic source of  $^{54}\text{Cr}$  does not significantly synthesize the other Cr isotopes and, therefore, variable contribution from a  $^{54}\text{Cr}$  producing source to the nascent solar system is not predicted to significantly modify the abundance of the remaining Cr isotopes. It is now firmly established that heterogeneity in  $^{54}\text{Cr}/^{52}\text{Cr}$  ratios exists between different bulk solar reservoirs<sup>6</sup>, which is thought to reflect admixing of variable amounts of pre-solar carriers heavily enriched in  $^{54}\text{Cr}$ <sup>11,12</sup>. The presence of nucleosynthetic  $^{54}\text{Cr}$  variability between different bulk solar system reservoirs provides a means to explore genetic relationships between early solar system condensates, diverse asteroids and the terrestrial planets<sup>6</sup>. However, the total range of known  $^{54}\text{Cr}$  variability in bulk meteorites is limited to only  $\sim 250$  ppm<sup>6</sup>. Thus, taking full advantage of potential  $^{54}\text{Cr}$  variability to track genetic relationships between early solar system reservoirs requires highly-precise  $^{54}\text{Cr}/^{52}\text{Cr}$  measurements.

<sup>a</sup>Centre for Star and Planet Formation, Natural History Museum of Denmark, University of Copenhagen, DK-1350, Copenhagen, Denmark; e-mail: schiller@snm.ku.dk

1  
2  
3 A minor additional component to the nucleosynthesis of  
4  $^{53}\text{Cr}$  comes from the decay of the short-lived radionuclide  $^{53}\text{Mn}$ <sup>13,44</sup>.  
5 With a half-life of 3.74 Ma, the  $^{53}\text{Mn}$ - $^{53}\text{Cr}$  decay system is  
6 a powerful chronometer to date asteroidal differentiation pro-  
7 cesses in the early solar system (e.g.,<sup>5,15,16</sup>). However, the  
8 relatively low initial solar system  $^{53}\text{Mn}/^{55}\text{Mn}$  ratio of  $\sim 6 \times$   
9  $10^{-6}$  (<sup>15</sup>) coupled with the relatively long half-life of the de-  
10 cay system result in  $^{53}\text{Cr}$  excesses in bulk basaltic meteorites  
11 that are typically less than 150 ppm (e.g.,<sup>5</sup>). Thus, similarly to  
12  $^{54}\text{Cr}$ , improving measurements of the radiogenic  $^{53}\text{Cr}$  compo-  
13 nent may allow for a refined chronology of early solar system  
14 events based on the  $^{53}\text{Mn}$ - $^{53}\text{Cr}$  system.

15  
16 Precise measurement of the radiogenic and nucleosynthetic  
17 components of Cr isotopes in meteoritic material has so far pri-  
18 marily been performed by thermal ionization mass spectrom-  
19 etry (TIMS). This approach allows for the analysis of small  
20 quantities of Cr on the order of 0.5-1  $\mu\text{g}$  with a typical ex-  
21 ternal reproducibility of 10-20 ppm for  $^{54}\text{Cr}/^{52}\text{Cr}$  ratios<sup>5,17-20</sup>,  
22 making the uncertainty a limiting factor in the resolution of po-  
23 tential small differences between distinct reservoirs. Moreover,  
24 significant improvement in Cr isotope measurements beyond  
25 the current state-of-the-art is limited by complications inherent  
26 to TIMS analyses such as, for example, filament poisoning and  
27 reservoir fractionation effects (e.g.,<sup>21</sup>). In contrast, isotope ra-  
28 tio measurements using multiple collector inductively coupled  
29 plasma mass spectrometry (MC-ICPMS) may allow for sig-  
30 nificant improvement in reproducibility owing to the sample-  
31 standard bracketing technique. Indeed, recent studies have demon-  
32 strated that is possible to obtain external reproducibilities be-  
33 low 5 ppm for the analysis of internally normalized Mg and Ca  
34 isotope ratios of chemically purified silicate matrices by MC-  
35 ICPMS<sup>22-26</sup>. Although some attempts have already been con-  
36 ducted to measure nucleosynthetic and radiogenic isotope ef-  
37 fects on  $^{53}\text{Cr}$  and  $^{54}\text{Cr}$  by MC-ICPMS<sup>16,27</sup>, the external repro-  
38 ducibility of these measurements have not been significantly  
39 improved compared to typical TIMS measurements. This pri-  
40 marily stems from the presence of irresolvable isobaric inter-  
41 ferences that affect the Cr mass array resulting from residual  
42 impurities in the Cr analyte solution such as, for example,  $^{50}\text{Ti}$ ,  
43  $^{50}\text{V}$  and  $^{54}\text{Fe}$ . Corrections for these isobaric interferences are  
44 much more important in MC-ICPMS work compared to TIMS  
45 given the high ionization efficiency of the plasma source. Ad-  
46 ditional isobaric interferences from molecular species include  
47 argon nitride ( $^{40}\text{Ar}^{14}\text{N}$ ) and oxide ( $^{40}\text{Ar}^{16}\text{O}$ ), which affect mass  
48  $^{54}\text{Cr}$  and  $^{56}\text{Fe}$ , respectively. Appropriate monitoring of the  $^{56}\text{Fe}$   
49 peak is critical to correct for any remaining Fe in the Cr solu-  
50 tion that may affect the measured  $^{54}\text{Cr}$  abundance via a direct  
51 isobar from  $^{54}\text{Fe}$ . Therefore, it is apparent that a prerequisite  
52 to high-precision Cr isotope analysis by MC-ICPMS is the ef-  
53 ficient removal of interferences and careful assessment of the  
54 accuracy of applied corrections.

55 Here we describe a novel analytical approach utilizing the

MC-ICPMS that addresses these issues and allows us to mea-  
56 sure the nucleosynthetic and radiogenic isotope effects on  $^{53}\text{Cr}$   
57 and  $^{54}\text{Cr}$  to a precision that is comparable to traditional TIMS  
58 analysis for similar sized samples and offers a significant im-  
59 provement where not sample limited. In addition, this approach  
60 allows for concurrent determination of the stable Cr isotopic  
composition of the sample allowing for better quality assess-  
ment of the data.

## 2 Analytical methods

### 2.1 Chromium separation from the sample matrix

Chromium occurs in nature either as trivalent Cr(III) or hex-  
avalent Cr(VI). The difference in valance state affects the ion  
chromatographic properties of Cr, which is commonly utilized  
to separate the two species (e.g.,<sup>28</sup>). Therefore, to maximize  
total Cr yields, care was taken to ensure the conversion of all  
Cr into the required oxidation state prior to each chemical sep-  
aration step. We describe below a four step column chromato-  
graphic procedure (summarized in Table 1) aimed at providing  
high Cr yields and efficient purification from matrix elements.

First, all samples were purified for Fe by passing the sample  
through AG1-X4 200-400 mesh anion resin in 6M HCl (Table  
1). The resin bed was typically 2 mL for sample sizes of 50  
mg. Cr was collected with the initial load and an additional 4  
mL of 6M HCl.

In a second step, total sample equivalents of 10 mg were  
passed through  $\sim 2$  mL of BioRad AG50W-X8 200-400 mesh  
resin. For larger samples, volumes were scaled accordingly.  
In preparation of this separation step, samples were fluxed for  
12h in 6M HCl to convert Cr to its trivalent form. The solution  
was diluted then to 0.5M HCl with distilled water and loaded  
onto the resin. The Cr cut was collected in the initial load and  
an additional 20 mL of 0.5M  $\text{HNO}_3$ . The remaining matrix was  
eluted from the column in 10 mL 6M HCl. To ensure near com-  
plete recovery of Cr in this step, the eluted matrix was collected  
and reprocessed through the same column and the Cr cuts from  
both elutions were combined.

Remaining trace amount of Ti and V were specifically tar-  
geted in the last two separation steps using Eichrom TODGA  
resin. The first TODGA resin step utilizes the high retention  
of Ti on the resin in concentrated  $\text{HNO}_3$ , while the second step  
takes advantage of the retention of V in 8M HCl<sup>29</sup>. Samples  
were loaded onto a 0.75 mL resin bed in a pipette tip column  
in 0.5 mL 14M  $\text{HNO}_3$  and Cr was collected in the load and an  
additional 4 mL of 14M  $\text{HNO}_3$ . Subsequently the resin was  
cleaned by alternate washing with distilled water, 6M HCl and  
7M  $\text{HNO}_3$ . Following this step, the Cr fraction was converted  
to chloride form and loaded in 0.5 mL 8M HCl onto the same  
resin bed. The Cr was collected with the load and an additional  
2 mL of 8M HCl.

Because any remaining trace of Fe in the sample requires significant interference corrections on  $^{54}\text{Cr}$ , samples were passed through a final anion chemistry identical to the first Cr separation step but using a smaller resin bed and elution volume of 0.25 mL and 3 mL, respectively. Each sample was monitored prior to analysis by MC-ICPMS for Fe concentration and samples that required more than 100 ppm correction on  $^{54}\text{Cr}$  from  $^{54}\text{Fe}$  were re-processed through the Fe separation step. Total procedural blanks of this procedure were on the order of a few ng of Cr and inconsequential for the measured isotopic composition considering the size of the samples and their Cr isotopic anomalies.

**Table 1** Four step Cr purification scheme for a 10 mg silicate sample.

Eluent	Vol. (mL) <sup>a</sup>	Elements eluted
<b>Step 1: Fe removal<sup>b</sup></b>		
6M HCl	2	Conditioning
Load sample in 6M HCl	1	
6M HCl	2	Cr + matrix
remaining on column		Fe
<b>Step 2: matrix removal<sup>c</sup></b>		
0.5M HCl	4	Conditioning
Load sample in 0.5M HCl	3	
0.5M HNO <sub>3</sub>	20	Cr
6M HCl	10	matrix
<b>Step 3: Ti removal<sup>d</sup></b>		
14M HNO <sub>3</sub>	4	Conditioning
Load sample in 14M HNO <sub>3</sub>	0.5	
14M HNO <sub>3</sub>	4	Cr
<b>Step 4: V removal<sup>d</sup></b>		
8M HCl	4	Conditioning
Load sample in 8M HCl	0.5	
8M HCl	2	Cr

<sup>a</sup> Volume of eluent. <sup>b</sup> Biorad Poly-Prep column with 2 mL AG1-X4 200-400 mesh resin. <sup>c</sup> Biorad Poly-Prep column with 2 mL of AG50W-X8 200-400 mesh resin. <sup>d</sup> Pipette tip column with 0.75 mL of TODGA resin. All resins are discarded after use.

## 2.2 Chromium isotope measurements by MC-ICPMS

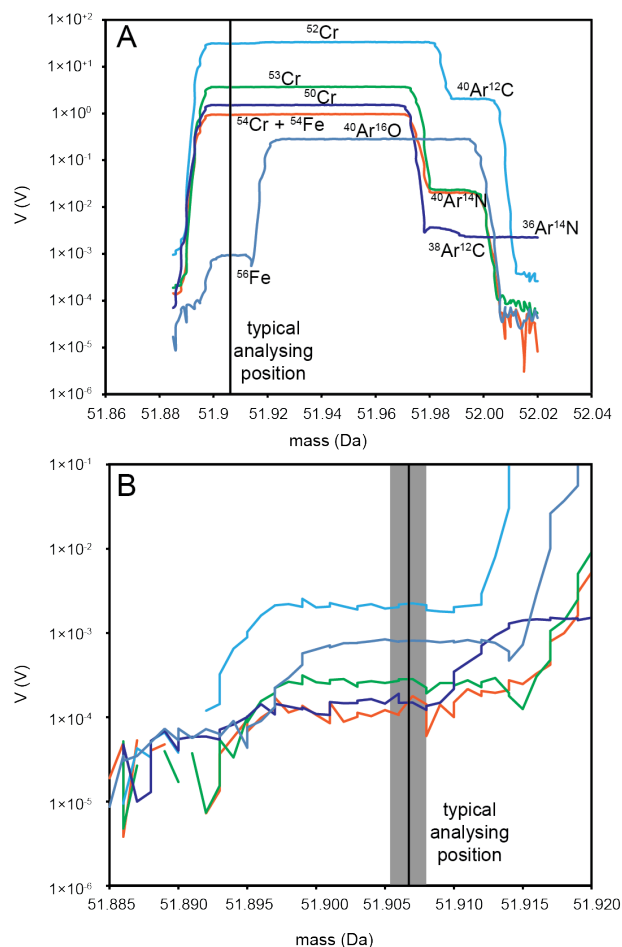
Chromium data was acquired with the ThermoFisher Neptune Plus MC-ICPMS located at the Centre for Star and Planet Formation (Natural History Museum of Denmark, University of Copenhagen). Because the gas based  $^{40}\text{Ar}^{16}\text{O}$  and  $^{40}\text{Ar}^{14}\text{N}$  interferences increase significantly when using high sensitivity cones such as the Jet sample cone and the skimmer X-cone offered by ThermoFisher, a lower sensitivity approach was taken

by combining a Jet sample cone in combination with a skimmer H-cone. This lowers the sensitivity by about 30% compared to a Jet sample cone and skimmer X-cone, but reduces oxide and nitride interferences by a factor of at least 2-3. To further reduce these interferences, samples were introduced to the plasma in 2.5% HNO<sub>3</sub> via an ESI Apex IR desolvating nebulizer with Trifluoro-methane (CHF<sub>3</sub>) as supplementary gas instead of using N<sub>2</sub>. Although the introduction of carbon creates a significant  $^{40}\text{Ar}^{12}\text{C}$  interference on  $^{52}\text{Cr}$ , the gas significantly reduces the nitride and oxide interferences and has a positive influence on overall signal sensitivity and stability. Optimal sensitivity combined with minimal oxide and nitride production was achieved by running in 'cold plasma' mode with an RF power of 600 to 800 W depending on daily tuning conditions. Under these analytical conditions, the  $^{40}\text{Ar}^{16}\text{O}$  and  $^{40}\text{Ar}^{14}\text{N}$  signals were typically below 0.5 V and 0.2 V, respectively, when using the high (16 μm) resolution slit of the Neptune. With this setup and a sample aspiration rate of ~60 μL/minute, a concentration of 1 ppm resulted in a  $^{52}\text{Cr}$  signal of ~30 V.

Chromium isotope data were acquired in static mode using seven Faraday collectors. Apart from the four Cr isotopes ( $^{50}\text{Cr}$ ,  $^{52}\text{Cr}$ ,  $^{53}\text{Cr}$ ,  $^{54}\text{Cr}$ ),  $^{49}\text{Ti}$ ,  $^{51}\text{V}$  and  $^{56}\text{Fe}$  were also monitored to correct for unresolvable isobaric interferences on  $^{50}\text{Cr}$  from  $^{50}\text{Ti}$  and  $^{50}\text{V}$  as well as on  $^{54}\text{Cr}$  from  $^{54}\text{Fe}$ . Faraday collectors were connected with  $10^{11}$  Ω feedback resistors for  $^{50}\text{Cr}$ ,  $^{53}\text{Cr}$ ,  $^{54}\text{Cr}$  and  $^{51}\text{V}$ . The largest beam  $^{52}\text{Cr}$  was monitored using a  $10^{10}$  Ω feedback resistor to allow for beam intensities larger than 50 V whereas low noise  $10^{12}$  Ω feedback resistors were used for measurement of the small  $^{49}\text{Ti}$  and  $^{56}\text{Fe}$  signals. Data was acquired on the low mass side of the Cr peak typically at a centre mass of 51.910 or ~0.030 atomic mass units (Da) from the peak centre using the 16 μm entrance slit with a resolving power ( $M/\Delta M$  as defined by the peak edge width from 5-95% full peak height) that was always greater than 8,000 for  $^{54}\text{Cr}$  to ensure a interference-free peak flat plateau. At this given resolution, this peak position allows to collect carbide, oxide and nitride interference-free signals for all Cr isotopes as well as  $^{49}\text{Ti}$ ,  $^{51}\text{V}$ , and  $^{56}\text{Fe}$  (Fig. 1).

Peak centres were performed only at the beginning of an analytical session and no peak drift was observed for sessions lasting more than a 48 h. Because the Neptune peak centre routine was applied to the  $^{52}\text{Cr}$  signal, which also comprised a 5-10%  $^{40}\text{Ar}^{12}\text{C}$  interference signal, slight differences in the peak centre position exist between different analytical sessions. Therefore, after determining the peak centre position, the position of the interference-free plateau was determined by measuring the Cr isotopic ratios across the low mass side of the Cr peak at different individual mass positions prior to each analytical sessions in a similar fashion as described in Weyer and Schwieters (2003)<sup>30</sup>. Based on this experiment, an ideal mass position for analysis was determined and used for the remain-





**Fig. 1** In (A) a typical peakscan of the Cr isotopes and  $^{56}\text{Fe}$  is shown with approximately 20 V on the  $^{52}\text{Cr}$  signal and when measuring under the analytical conditions described in the text. (B) Depicts the interference area of the Cr peak at the low mass end when measuring the blank solution. Indicated in both figures is the approximate mass position at which the isotopic measurement was typically conducted.

der of individual analytical sessions.

Samples were typically analysed at a  $^{52}\text{Cr}$  signal intensity of 100 V and beam intensities of standard and sample were matched within 5% of each other. Each analysis comprised a total of 1259 s of combined wash out and baseline measurements obtained on-peak (in the same 2.5%  $\text{HNO}_3$  solution used to dissolve samples and standards) and 1667 s of data acquisition (100 scans integrated over 16.67 s). In between each step the auto sampler probe was cleaned for 30 s in a rinse solution of same molarity. From the 1259 s of data collected in the on-peak zero solution, only the last 800 s were used as baseline measurement. This approach allowed close monitoring of the wash out behaviour of sample and standard. Where sufficient Cr is available, samples were systematically analysed 10 times

over a time span of  $\sim 18$  h consuming a total of 30 to 60  $\mu\text{g}$  Cr.

### 2.3 Data reduction

All data reduction was conducted off-line using the freely available Iolite<sup>31</sup> data reduction software that runs within Igor Pro. The Cr data reduction module used for the data reported here can be freely obtained from the authors on request. Background intensities were interpolated using a smoothed cubic spline, as were changes in mass bias with time. Iolites ‘Smooth spline auto’ choice was used in all cases, which determines a theoretically optimal degree of smoothing based on variability in the reference standard throughout an analytical session. For all reported data the baseline subtraction was conducted using the ‘automatic’ spline option of Iolite, while standard interpolation was done using the ‘Smooth spline auto’ option. Stable isotope ratios are reported in the  $\delta$  notation according to the following formula:

$$\delta^X\text{Cr} [\text{‰}] = \left[ \frac{(\text{XCr}/^{52}\text{Cr})_{\text{sample}}}{(\text{XCr}/^{52}\text{Cr})_{\text{SRM979}}} - 1 \right] \times 10^3, \quad (1)$$

where x is either 50, 53 or 54. The mass-independent component of  $^{53}\text{Cr}$  ( $\mu^{53}\text{Cr}$ ) and  $^{54}\text{Cr}$  ( $\mu^{54}\text{Cr}$ ) is reported in the same fashion, but in the  $\mu$  notation as parts per million (ppm) instead of parts per thousand (‰). We use mass-independent as a generic term to describe radiogenic ingrowth on  $^{53}\text{Cr}$ , nucleosynthetic anomalies on  $^{54}\text{Cr}$  or, alternatively, inappropriate mass fractionation correction on both  $^{53}\text{Cr}$  and  $^{54}\text{Cr}$ . However, we emphasize that latter is in fact an apparent mass-independent effect, as it reflects an artefact of using an inappropriate mass fractionation law to account for a mass dependent process. The reported mass-independent component is the deviation from the internally normalized  $^{53}\text{Cr}/^{52}\text{Cr}$  and  $^{54}\text{Cr}/^{52}\text{Cr}$  of the sample from the reference standard (SRM 979), normalized to a  $^{50}\text{Cr}/^{52}\text{Cr} = 0.051859$  (<sup>32</sup>) using the exponential mass fractionation law.

## 3 Discussion

### 3.1 Reduction of gas based interferences

A major challenge when measuring Cr isotopes with an Ar-based plasma are the isobaric molecular interferences resulting from the Ar gas. In particular,  $^{40}\text{Ar}^{16}\text{O}$  and  $^{40}\text{Ar}^{14}\text{N}$  are troublesome because they interfere on the masses 54 and 56 and, thus, resolving these interferences is necessary for acquiring precise and accurate  $^{54}\text{Cr}$  data. As such, we focused on minimizing the contribution of molecular argon species to the Cr mass array. This was achieved by taking several steps: 1) Instead of using the highest sensitivity sample introduction sampler and skimmer cone setup of the Neptune Plus, a combina-

tion of Jet and X-cone, we opted for a somewhat less sensitive combination of Jet sampler cone and H skimmer cone. This results in at least 30 % sensitivity loss for the Cr signal, but reduces the oxide and nitride production rate by a factor of 2-3, effectively improving the sample over oxide and nitride signal. 2) Reduction of the RF power has long been known to be an effective mechanism to reduce the oxide production rate (e.g.,<sup>33</sup>). In the case of our approach measuring Cr isotopes, a lower RF power of 700 W compared to the usually applied 1200 W also resulted in a slight sensitivity improvement of the Cr signal of 10 to 20 %, while suppressing the oxide and nitride production by a factor of ~2-3) Finally, the usual additive gas of the Apex sample introduction system is N<sub>2</sub>. While addition of an additive gas is not essentially required, it does improve signal stability and can enhance the sensitivity of the system. However, considering that one of the biggest challenges in measuring a precise <sup>54</sup>Cr signal is resolving the <sup>40</sup>Ar<sup>14</sup>N interference, unnecessary addition of N<sub>2</sub> is counter-productive. To circumvent this problem, we turned to Trifluoromethan (CF<sub>3</sub>H) as an additive gas. A positive effect on the reduction of molecular interferences through the addition of CF<sub>3</sub>H to the Ar plasma has previously been reported<sup>34</sup> and can also be observed for <sup>40</sup>Ar<sup>14</sup>N and <sup>40</sup>Ar<sup>16</sup>O. However, the additional introduction of CF<sub>3</sub>H produces also a significant <sup>40</sup>Ar<sup>12</sup>C interference on mass 52. Fortunately, this interference requires the lowest mass resolving power of the three discussed molecular interferences and it is also an isobar on the most abundant Cr isotope, which results in a favourable signal to isobar ratio. The <sup>40</sup>Ar<sup>12</sup>C signal was typically between 5 and 15 V compared to a <sup>52</sup>Cr signal of 40 to 100 V. When using the high or medium resolution slits of the Neptune Plus, it is possible to obtain an interference-free plateau of 5 to 10 milli mass units on the low mass side of the peak. The position of and centre of this plateau was determined prior to each analytical session.

### 3.2 Correction of atomic isobaric interferences

Because the Ar plasma has a very high ionization efficiency, another critical step in acquiring accurate Cr isotope data by MC-ICPMS is an effective correction for the atomic isobaric interferences <sup>49</sup>Ti, <sup>51</sup>V, and <sup>56</sup>Fe, which cannot be resolved. The effect of these isobars is slightly different because the presence of Ti and V interferes on the mass bias correcting isotope <sup>50</sup>Cr and affects all measured Cr isotope ratios, while the presence of Fe solely affects the <sup>54</sup>Cr data. In order to test the accuracy of the interference corrections, a Cr ICPMS standard solution was doped separately with Ti, V and Fe at a level significantly larger than that of any sample after chemical Cr purification.

For Ti, the <sup>50</sup>Ti interference was subtracted from <sup>50</sup>Cr by calculating a mass-bias corrected <sup>50</sup>Ti signal from the measured <sup>49</sup>Ti beam. For mass-bias correction a <sup>50</sup>Ti/<sup>49</sup>Ti = 0.97377 (<sup>35</sup>) was inferred and the fractionation factor was derived from the

<sup>53</sup>Cr/<sup>52</sup>Cr-ratio that is free of isobaric interferences using a natural ratio of 0.11339 assuming a negligible difference in the mass fractionation behaviour of Ti and Cr. Because <sup>53</sup>Cr can be affected by decay of <sup>53</sup>Mn, this correction scheme is only robust for samples with small Mn/Cr ratios (and <sup>53</sup>Cr anomalies of less than a few hundred ppm) or that formed after extinction of <sup>53</sup>Mn (such as all terrestrial rocks). For samples where <sup>53</sup>Cr anomalies are significant and result in noticeable effects in the mass bias correction, an iterative approach can be taken with an initial correction of <sup>50</sup>Cr and then a secondary mass bias correction using the preliminary corrected <sup>50</sup>Cr/<sup>52</sup>Cr-ratio for precise determination of the size of the <sup>50</sup>Ti interference.

The Ti correction was tested by measuring a Cr solution containing a contribution of <sup>50</sup>Ti of more than 1609 ppm to the <sup>50</sup>Cr signal (Table 2), which is at least a factor of ten larger than that measured for natural samples processed through the Cr purification, versus the pure Cr solution. Prior to interference correction this amount of Ti resulted in apparent excesses in the mass bias corrected  $\mu^{53}\text{Cr}$  and  $\mu^{54}\text{Cr}$  of +777.2 and +1532.2, respectively. After correction both  $\mu^{53}\text{Cr}$  and  $\mu^{54}\text{Cr}$  were +1.2±2.2 and +3.6±2.6 (uncertainties are 2 se if not stated otherwise), respectively, within analytical uncertainty of zero when considering the external reproducibility of our approach (see below). Given the fact that the Ti concentration in this test exceeds that of typical samples after Cr purification by more than one order of magnitude, we feel confident that no bias during sample analysis is introduced from the Ti correction.

The correction of a potential vanadium contribution to the <sup>50</sup>Cr signal was conducted by calculating a <sup>50</sup>V signal based on <sup>51</sup>V assuming a natural <sup>50</sup>V/<sup>51</sup>V of  $2.425 \times 10^{-3}$  (<sup>36</sup>). Correction of mass bias experienced by <sup>51</sup>V in the MC-ICPMS and signal subtraction of the calculated <sup>50</sup>V beam contributing to <sup>50</sup>Cr was done in the same manner as for Ti. A similar V interference test as for Ti was conducted to verify the accuracy of the approach. For this a Cr solution containing a ~24 ppm contribution of <sup>50</sup>V to the <sup>50</sup>Cr signal was measured versus a pure Cr solution (Table 2). The tested V contribution is much smaller than that of the Ti test given the much lower natural abundance of the <sup>50</sup>V isotope (<sup>51</sup>V/<sup>50</sup>V ~ 400). As a result, the apparent excesses on both  $\mu^{53}\text{Cr}$  and  $\mu^{54}\text{Cr}$  of +10.2 ± 2.6 and +24.9 ± 2.9, respectively, are also small but resolvable. No apparent excesses remained after the V correction with  $\mu^{53}\text{Cr}$  and  $\mu^{54}\text{Cr}$  of -0.4 ± 2.1 and -0.3 ± 1.7, respectively (Table 2).

Lastly, the correction for the isobaric Fe interference on <sup>54</sup>Cr was tested. The correction for any contribution of <sup>54</sup>Fe to the <sup>54</sup>Cr signal is non-trivial because the geometry of the Neptune Plus does not allow to measure the relatively interference-free <sup>57</sup>Fe simultaneously with all Cr isotopes and <sup>49</sup>Ti. Instead this correction must be based on <sup>56</sup>Fe. A Fe correction using <sup>56</sup>Fe is complicated by the typically large isobaric <sup>40</sup>Ar<sup>16</sup>O interference and hence requires careful assessment.

## 3.3 Reproducibility and comparison with previous data

## 3 DISCUSSION

**Table 2** Summary of interference correction tests performed on pure SRM 979 Cr standard doped with single element solutions of Ti, V, and Fe. Shown uncertainties are the 2 se of the replicate analyses.

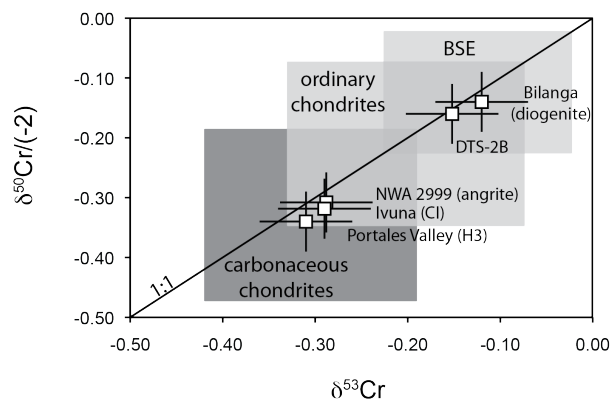
Isobar	Inf. Contrib. (ppm)	$\mu^{53}\text{Cr}_{\text{uncor.}}$ (ppm)	$\mu^{54}\text{Cr}_{\text{uncor.}}$ (ppm)	$\mu^{53}\text{Cr}_{\text{cor.}}$ (ppm)	$\mu^{54}\text{Cr}_{\text{cor.}}$ (ppm)	n
$^{50}\text{Ti}$	1609.2	+777.2±2.0	+1532.2±2.1	+1.2±2.2	+3.6±2.6	10
$^{50}\text{V}$	23.6	+10.2±2.6	+24.9±2.9	-0.4±2.1	-0.3±1.7	10
$^{54}\text{Fe}$	558.1	+1.4±1.8	+555.7±4.6	+1.7±2.1	+1.2±2.3	10

While the mass resolution of the Neptune does in principle allow to fully resolve  $^{56}\text{Fe}$  and  $^{40}\text{Ar}^{16}\text{O}$ , the interference is significantly larger by orders of magnitude than the  $^{56}\text{Fe}$  signal. Thus, even small tailing contributions of  $^{40}\text{Ar}^{16}\text{O}$  can lead to overcorrection and additional noise in the calculated  $^{54}\text{Fe}$  signal. Because no Fe isotope interferes with the  $^{50}\text{Cr}$  and  $^{52}\text{Cr}$  signals, the contribution of  $^{54}\text{Fe}$  to the  $^{54}\text{Cr}$  signal was calculated using a Ti and V corrected  $^{50}\text{Cr}/^{52}\text{Cr}$  for mass bias correction and natural isotope abundance fraction of 0.05845 and 0.91754 for  $^{54}\text{Fe}$  and  $^{56}\text{Fe}$ , respectively<sup>37</sup>. Similar to the tests for Ti and V, a pure Cr solution was doped with Fe at a level that significantly exceeds that of purified Cr samples and was measured versus a pure solution to test the accuracy of the applied correction. In the test, the  $^{54}\text{Fe}$  contribution to the  $^{54}\text{Cr}$  signal was calculated to be 558.1 ppm, compared to typically less than 50 ppm for purified Cr samples. Prior to the interference correction, this resulted in an apparent excess on  $\mu^{54}\text{Cr}$  of  $+555.7 \pm 4.6$  that was fully corrected for to  $+1.2 \pm 2.3$  through the Fe-subtraction. At this iron concentration, the interference correction is also the only one of the tested atomic interferences where the uncertainty in the isotope ratio used for correction has a quantifiable effect (3 ppm) on the final corrected  $\mu^{54}\text{Cr}$  and could potentially introduce a bias to the data. However, the successful correction to within uncertainty of zero demonstrates that even large contributions of Fe to the Cr signal can be completely corrected for and no resolvable bias is introduced in the calculated  $\mu^{54}\text{Cr}$  composition by the applied isotope ratios for interference correction.

## 3.3 Reproducibility and comparison with previous data

**3.3.1 Cr stable isotope data.** High precision chromium stable isotope data is already routinely collected by MC-ICPMS (e.g.,<sup>38–40</sup>). Based on all repeat measurements presented in this study (Table 3), the sample-standard bracketing approach taken here results in a similar reproducibility of 0.05‰/Da compared to that of studies using either standard-sample bracketing<sup>39</sup> or the use of a Cr double spike<sup>38</sup>. The  $\delta^{53}\text{Cr}$  offset of  $-0.152 \pm 0.045$  for the DTS-2B dunite standard with respect to SRM 979 is in excellent agreement with that of terrestrial igneous silicates of  $-0.124 \pm 0.101$  determined by Schönberg et al.<sup>38</sup>. The  $\delta^{53}\text{Cr}$  of  $-0.290 \pm 0.010$  and  $-0.310 \pm 0.010$  for the CI chondrite Ivuna and the H6 chondrite Portales Valley, respec-

tively, analysed here are also in good agreement with that of the average carbonaceous [ $-0.31 \pm 0.11$  (2sd)] and ordinary [ $-0.20 \pm 0.13$  (2sd)] chondrites (Fig. 2)<sup>40</sup>.



**Fig. 2** Stable isotope data ( $\delta^{53}\text{Cr}$  and  $\delta^{50}\text{Cr}$  normalized to represent one atomic mass unit difference from the normalizing isotope) for meteorites compared with that of published values. Data for BSE is from<sup>38</sup> and that for ordinary and carbonaceous chondrites was taken from<sup>40</sup>.

The  $\delta^{53}\text{Cr}$  composition of the diogenite Bilanga ( $-0.120 \pm 0.010$ ) is indistinguishable from that of DTS-2B and bulk silicate Earth (BSE; Fig. 2). In contrast, the NWA 2999 angrite has a lighter  $\delta^{53}\text{Cr}$  of  $-0.288 \pm 0.027$ , which is comparable to chondrites. The compositional difference between Bilanga and NWA 2999, which are both products of differentiated planetesimal, is surprising because an isotopically heavier stable Cr composition of BSE with respect to chondrites has been used to argue for Cr isotope fractionation during low temperature parent body differentiation on planetary embryos<sup>40</sup>. In particular, Moynier et al. suggested that the oxygen fugacity may play a role in the isotopic fractionation with higher fugacity imparting larger isotopic fractionation during metal-silicate differentiation. This, however, is not supported by the stable isotopic composition of the Bilanga and NWA 2999 meteorites coupled with estimates of the oxygen fugacity during angrite and eucrite formation, which appear to have been more oxidising on the angrite parent body<sup>41</sup>. Considering that no single type of chondrite can explain the chemical and isotopic composition of the Earth<sup>42</sup>, this suggests that differences in the sta-

ble isotopic composition of Cr between meteorites and Earth are not predominantly controlled by metal-silicate fractionation but are instead the product of differences in the stable isotopic composition of their precursor material. This scenario is apparently consistent with the lack of Cr isotope homogenisation amongst bulk solar system reservoirs as evidenced by the presence of widespread  $^{54}\text{Cr}$  nucleosynthetic heterogeneity<sup>6</sup>. In agreement with earlier work<sup>39</sup>, we conclude that accurate and reproducible stable Cr isotope data can be obtained by standard-sample bracketing using MC-ICPMS. Moreover, the lack of an isotopically enriched spike in our approach offers the possibility to concurrently determine stable, radiogenic and nucleosynthetic isotope effects, which are of particular interest in cosmochemistry.

**3.3.2 Mass-independent data.** As discussed earlier, the mass-independent composition of  $^{53}\text{Cr}$  ( $\mu^{53}\text{Cr}$ ) and  $^{54}\text{Cr}$  ( $\mu^{54}\text{Cr}$ ) are of particular interest in meteoritic materials as they provide time information and trace potential genetic relationships amongst early solar system reservoirs, respectively. Thus, improving the precision and accuracy of  $\mu^{53}\text{Cr}$  and  $\mu^{54}\text{Cr}$  data is the focus of the technique described here. The external reproducibility was determined by repeated analysis of a pure Cr ICPMS standard solution (Peak Performance) and Cr chemically purified from the USGS dunite DTS-2B rock standard, which were both measured against the SRM 979 Cr isotopic standard. However, the Peak Performance and SRM 979 standards contained traces of Fe at a concentration equivalent to a few hundred ppm correction on  $^{54}\text{Cr}$ . Thus, the SRM 979 was purified for Fe through step 1 of the Cr separation procedure described here. No such clean up was conducted for the Peak Performance Cr standard as this was used as an additional measure to test the reproducibility of a 'dirty' sample. However, we emphasize that the traces of Fe present in the Peak Performance standard are in much greater concentration (by a factor of  $\sim 10$ ) compared to that remaining in the natural samples analyzed in this study. Repeated analysis of the Peak Performance Cr ICPMS solution including the contaminant tests with variable concentrations of interfering elements versus a pure Peak Performance solution ( $n = 4$ ) resulted in  $\mu^{53}\text{Cr}$  and  $\mu^{54}\text{Cr}$  of  $+0.3 \pm 2.7$  (2 sd) and  $+1.4 \pm 3.3$  (2 sd), respectively, indistinguishable from zero. While this represents near ideal conditions (no chemical separation procedure), it offers an indication of the best possible accuracy that can be obtained by MC-ICPMS using the analytical conditions employed in this study.

The Cr Peak Performance solution was also measured versus the purified SRM 979 standard. This test reveals a difference in the stable isotopic composition of  $\delta^{53}\text{Cr} = +0.154 \pm 0.011$  between these two standard solutions (Table 3). Further, when the kinetic (=exponential) law is used for the correction of mass discrimination experienced by the standard solutions

a difference in  $\mu^{53}\text{Cr} = -7.8 \pm 2.6$  and  $\mu^{54}\text{Cr} = -17.2 \pm 5.8$  is obtained, indicating that the law used for mass discrimination is not appropriate to correct for the stable isotope difference between these two standards<sup>43</sup>. The stable isotope fractionation between the two standards is better, but not perfectly, described by a mass-dependence that follows the equilibrium law, which results in  $\mu^{53}\text{Cr} = -3.2 \pm 2.6$  and  $\mu^{54}\text{Cr} = -4.2 \pm 5.8$ . These  $\mu^{53}\text{Cr}$  and  $\mu^{54}\text{Cr}$  values indicate that the difference in the stable isotope compositions between the two standards reflects predominantly variable equilibrium isotope fractionation during production of the standards. When comparing the isotopic composition of both SRM 979 and Peak Performance standards to DTS-2B, which is a good representation of the Cr isotopic composition of BSE, it is evident that both standards experienced equilibrium isotope fractionation but to a variable degree (Table 3). Importantly, the different stable isotope compositions and the systematic offset between DTS-2B and SRM 979 of  $\mu^{53}\text{Cr} = 3.8 \pm 1.3$  and  $\mu^{54}\text{Cr} = 7.9 \pm 5.7$  can also, in part, be explained by loss of Cr through an equilibrium process experienced by SRM 979 during its production. The presence of resolvable fractionation effects in the Cr standards highlights the significance of the precise and accurate isotopic characterization of the Cr isotope standard used in future studies. For example, although this issue has recently been recognized<sup>18</sup>, little attention has been paid to the isotopic composition of the Cr standard used for comparison to meteoritic samples in earlier studies<sup>5,6,17,27,44,45</sup>, allowing for potential biases in the data and complicating a detailed comparison.

The most reliable assessment of the external reproducibility of our technique comes from measurements of Cr purified from multiple individually processed aliquots of the DTS-2B standard versus SRM 979 (Table 3). In fact, the reproducibility obtained for these samples is similar or better than that achieved for repeat measurements of pure standard solutions, indicating that no variable bias was introduced through the chemical purification procedure. In combination with all repeat measurements of Cr standards performed in this study, the repeated analyses of DTS-2B indicate that it is possible to achieve an external reproducibility that is better than 2.5 and 5.8 for  $\mu^{53}\text{Cr}$  and  $\mu^{54}\text{Cr}$ , respectively. This represents a two-fold improvement compared to all earlier published work.

To further assess the accuracy of our approach, we also measured the Cr isotopic composition of four meteorites that have a known range of nucleosynthetic  $^{54}\text{Cr}$  anomalies<sup>6,18,20</sup>. Within uncertainties, all four samples have  $^{54}\text{Cr}$  anomalies that are in agreement with published data. A good correlation and no resolvable systematic bias between the new high precision data and previously published data for the same meteorite or class of meteorite exists (Fig. 3), suggesting that our measurements are accurate to the stated uncertainties for samples with very distinct matrices.

Comparison of  $\mu^{53}\text{Cr}$  for the analysed meteorites is com-



## 3.4 Precision for small sample sizes

## 3 DISCUSSION

**Table 3** Stable and mass-independent Cr isotope data for standards and meteorites. Shown uncertainties are the 2 se of the replicate analyses.

Sample	Type	$\delta^{50}\text{Cr}$ (‰)	$\delta^{53}\text{Cr}$ (‰)	$\delta^{54}\text{Cr}$ (‰)	$\mu^{53}\text{Cr}$ (ppm)	$\mu^{54}\text{Cr}$ (ppm)	n	$^{55}\text{Mn}/^{52}\text{Cr}$
vs. Peak Performance:								
Cr Peak Perf.	Cr standard	+0.003±0.007	-0.003±0.003	-0.002±0.006	-1.2±2.2	+1.0±2.5	10	—
Cr+Ti Peak Perf.	Cr standard	-0.017±0.031	+0.008±0.015	+0.019±0.030	+1.2±2.2	+3.6±2.6	10	—
Cr+V Peak Perf.	Cr standard	+0.018±0.006	-0.009±0.003	-0.018±0.008	-0.4±2.1	-0.3±1.7	10	—
Cr+Fe Peak Perf.	Cr standard	+0.020±0.012	-0.007±0.007	-0.017±0.012	+1.7±2.1	+1.2±2.3	10	—
<i>average and 2sd</i>		<i>+0.006±0.034</i>	<i>-0.003±0.015</i>	<i>-0.002±0.034</i>	<i>+0.3±2.7</i>	<i>+1.4±3.3</i>	4	—
vs. SRM 979:								
Cr PeakPerf.	Cr standard	-0.340±0.039	+0.160±0.020	+0.310±0.041	-9.0±2.2	-20.3±4.2	10	—
Cr PeakPerf.	Cr standard	-0.327±0.047	+0.150±0.023	+0.300±0.049	-8.0±1.4	-16.9±1.8	10	—
Cr PeakPerf.	Cr standard	-0.323±0.043	+0.152±0.022	+0.299±0.045	-6.4±1.6	-14.5±2.7	10	—
<i>average and 2sd</i>		<i>-0.330±0.018</i>	<i>+0.154±0.011</i>	<i>+0.303±0.012</i>	<i>-7.8±2.6</i>	<i>-17.2±5.8</i>	3	—
DTS-2B 1	dunite	+0.325±0.008	-0.156±0.003	-0.307±0.010	+3.5±1.1	+8.4±3.2	10	—
DTS-2B 2	dunite	+0.385±0.009	-0.183±0.003	-0.360±0.010	+3.6±2.0	+8.9±3.0	10	—
DTS-2B 3	dunite	+0.276±0.019	-0.132±0.010	-0.270±0.017	+3.4±1.5	+3.8±4.1	10	—
DTS-2B 4	dunite	+0.294±0.013	-0.139±0.008	-0.274±0.013	+4.8±1.5	+10.4±2.8	10	—
<i>average and 2sd</i>		<i>+0.320±0.096</i>	<i>-0.152±0.045</i>	<i>-0.303±0.083</i>	<i>+3.8±1.3</i>	<i>+7.9±5.7</i>	4	—
Ivuna	CI	+0.637±0.019	-0.290±0.010	-0.445±0.011	+16.4±2.0	+155.2±4.8	10	0.748±0.003
Portales Valley	H	+0.680±0.010	-0.310±0.010	-0.690±0.010	+15.2±2.0	-39.4±4.0	10	0.797±0.004
Bilanga	diogenite	+0.280±0.010	-0.120±0.010	-0.340±0.010	+15.0±2.4	-62.6±3.8	10	0.653±0.002
NWA 2999	angrite	+0.616±0.054	-0.288±0.027	-0.640±0.053	+10.2±2.2	-49.5±4.5	10	0.802±0.003

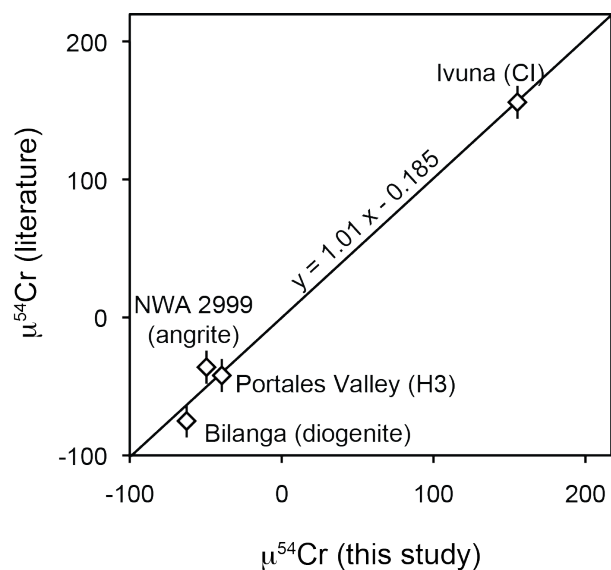
plicated by differences in the standards used, secondary corrections in older literature and divergent  $^{55}\text{Mn}/^{53}\text{Cr}$  ratios. Previous data for CI chondrites appear to be bimodal with average values of  $\sim+23$  (<sup>15,18</sup>) and  $\sim+43$  (<sup>16,20</sup>) for reasons that are not clear but could be related to distinct Cr isotopic compositions of the respective standards used (e.g.,<sup>18</sup>). Our value of  $+16.4 \pm 2.0$  for the CI chondrite Ivuna is at the lower range of the lower estimates for this type of meteorite. However, we also measured a  $^{55}\text{Mn}/^{53}\text{Cr}$  for our sample that is slightly lower ( $\sim 15\%$ ) than the inferred bulk rock composition of this meteorite. Therefore, our data for Ivuna agrees well with that for the same type of meteorite determined by<sup>15,18</sup> but not with that of<sup>16,20</sup>. Very good agreement of the measured  $\mu^{53}\text{Cr}$  exists for the H chondrite Portales Valley and the diogenite Bilanga with published values for meteorites of the same type<sup>15,18</sup>. No published  $\mu^{53}\text{Cr}$  bulk data for NWA 2999 is available, although the smaller  $\mu^{53}\text{Cr}$  excess compared to Bilanga is apparently consistent with the relatively young age of this angrite<sup>46</sup>.

### 3.4 Precision for small sample sizes

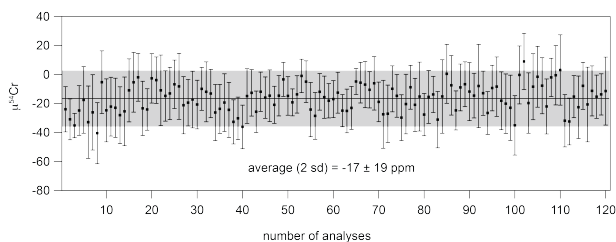
The high-precision Cr isotope analysis described here takes advantage of the relatively high Cr concentration of bulk meteorites and, therefore, large amounts of Cr are typically available for analysis. However, when aiming to analyse, for exam-

ple, individual components in chondrites such as chondrules or refractory inclusions, the amount of available Cr is generally only in the order of a few  $\mu\text{g}$  or less. For such sample sizes, traditional TIMS measurements are well-suited although each individual measurement with uncertainties of  $\sim 20$  ppm on  $^{54}\text{Cr}$  requires several hours of machine time. On the other hand, single sample analysis of our method consumes between 3-6  $\mu\text{g}$  of Cr, but results in uncertainties of  $\sim 10$  ppm within  $\sim 1.5$  hours when including the bracketing standard analyses. Thus, the MC-ICPMS potentially provides a much higher throughput of samples with comparable reproducibility.

To evaluate the external reproducibility of our methods for small sample sizes, we reprocessed our Peak Performance versus SRM 979 data and divided the individual 1660 s Peak Performance sample analyses into 4 segments of 415 s to simulate a Cr consumption of  $\sim 1$   $\mu\text{g}$  per individual sample measurement, while SRM 979 standard and baseline measurements were left unchanged (Fig. 4). The reproducibility reached in this test for  $\mu^{54}\text{Cr}$  of 120 individual sample measurements is 19 ppm (2 sd). This shows that our approach using MC-ICPMS results in comparable precision to measurements of similar amounts of Cr by TIMS, but with MC-ICPMS analysis being significantly faster and yielding additional stable isotope information.



**Fig. 3** Comparison of measured  $^{54}\text{Cr}$  for different meteorites with that published for the same type of meteorite. Also shown is a linear fit to the data approximating a 1:1 correlation. Data from<sup>6</sup>.

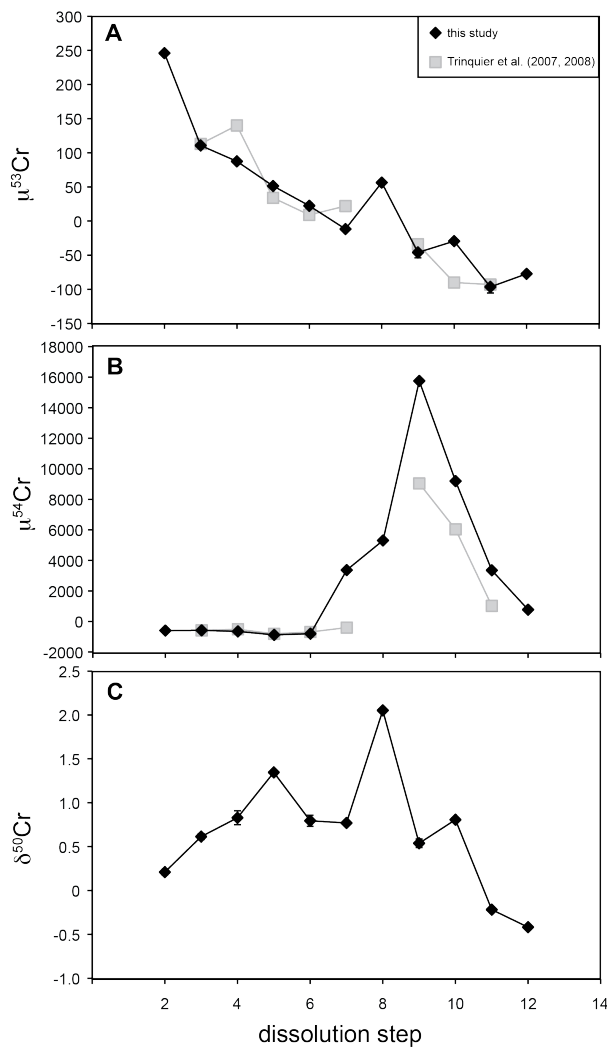


**Fig. 4** Data for  $\mu^{54}\text{Cr}$  from three individual measurements of Peak Performance ICPMS Cr standard solution versus SRM 979 (Table 3) shown as individual measurements of 415 s of data acquisition or representing  $\sim 1 \mu\text{g}$  Cr consumed during each analysis. Indicated in grey is the 2 sd of all data.

### 3.5 Acid stepwise dissolution of the Ivuna CI chondrite

As part of the analytical development for the methods presented here, we measured Cr extracted from eleven separates from a stepwise dissolution experiment of the Ivuna CI chondrite that have previously been analysed for the isotopic composition of other elements<sup>47</sup>. The presence of distinct presolar carrier phases of chromium isotopes in primitive chondrites such as Ivuna has been identified in a number of studies using a similar approach, which results in the crude separation of different mineralogical components within a meteorite according to their acid resistance<sup>1,6,15</sup>. Because this produces a wide spread in the isotopic and chemical composition of each step, comparison with previous results for the step wise dissolution provides a good test of our analytical method. In addition, the stable isotope data obtained in our study provides additional informa-

tion that was previously not available. Because this data was produced as part of the development of the analytical protocol developed here, some of the data have been measured with a lower degree of precision and have larger attached uncertainties (Table 4).



**Fig. 5** Shown are the  $\mu^{53}\text{Cr}$  (A),  $\mu^{54}\text{Cr}$  (B), and  $\delta^{50}\text{Cr}$  (C) data of the step wise dissolution experiment of the CI chondrite Ivuna. Detailed information about the applied procedure can be found in Paton et al.<sup>47</sup>. Similar data for an experiment using the CI chondrite Orgueil from Trinquier et al.<sup>6</sup> are also shown for comparison.

We compare in Figure 5 our new results for this experiment with previously published Cr isotopic data for the CI chondrite Orgueil obtained by TIMS<sup>6</sup>. Although there are differences in the size of the dissolved sample and the exact number of leaching steps, both data sets follow the same isotopic trends, indicating that the  $^{53}\text{Cr}$  and  $^{54}\text{Cr}$  obtained by MC-ICPMS and TIMS are comparable. In detail, the higher resolution dissolu-

**Table 4** Stable and mass-independent Cr isotope data for the step wise dissolution experiment of the CI chondrite Ivuna. Shown uncertainties are the 2 se of the replicate analyses except where stated otherwise. Uncertainties for calculated bulk composition were determined by Monte Carlo simulation using uncertainties on shown isotope ratios and assuming a 10% uncertainty on the absolute Cr abundance.

wt.% Cr	Step	$\mu^{50}\text{Cr}$	$\mu^{53}\text{Cr}$	$\mu^{54}\text{Cr}$	n	$^{55}\text{Mn}/^{52}\text{Cr}$
<0.1	L1	-	-	-	-	44
0.1	L2	+0.210±0.130	+246±20	-592±17	4	189
14.9	L3	+0.614±0.031	+110.7±2.3	-579±5.2	5	1.79
2.1	L4	+0.829±0.033	+87.5±4.6	-649±10	5	3.86
7.3	L5	+1.346±0.079	+51.4±1.3	-876±10	5	0.58
48.8	L6	+0.795±0.010	+22.4±1.5	-799±2.9	10	0.21
1.4	L7	+0.770±0.064	-11.7±3.9	+3369±19	5	1.27
0.5	L8	+2.052±0.015	+56.4±2.0	+5306±8.7	5	2.47
0.9	L9	+0.538±0.008	-46.0±1.6	+15753±8.5	10	1.53
4.3	L10	+0.807±0.049	-29.4±7.9	+9194±19	5	0.07
7.7	L11	-0.218±0.007	-96.5±0.7	+3353±5.0	4	0.09
11.8	L12	-0.418±0.007	-77.3±8.4	+777±8.8	5	0.11
	<i>calc. bulk</i> ( $\pm 2$ <i>sd</i> )	+0.590±0.08	+15.0±5.4	413±129		0.73

tion experiment employed here displays larger  $\mu^{54}\text{Cr}$  excesses, whereas the deficits are nearly indistinguishable. The larger excesses may point to a better preservation of the carriers of anomalous  $^{54}\text{Cr}$  in Ivuna compared to Orgueil. A better preservation of the  $^{54}\text{Cr}$  carrier is also supported by the observation that the  $\mu^{53}\text{Cr}$  data of both meteorites, although measured by different methods, are in excellent agreement with each other. Mass balance calculations further indicate that both  $\mu^{53}\text{Cr}$  and  $\delta^{50}\text{Cr}$  are indistinguishable from that of the bulk measurement. The calculated bulk  $\mu^{54}\text{Cr}$  composition of Ivuna ( $413 \pm 129$ ) is more positive than the measured bulk composition ( $155.2 \pm 4.8$ ). Most likely, this overestimation is caused by inaccuracies in determining the absolute Cr abundance in each leaching step. Because variations in the individual  $\mu^{54}\text{Cr}$  composition of the dissolution steps are more than ten times larger than those of  $\mu^{53}\text{Cr}$  and  $\delta^{50}\text{Cr}$ , the recalculated bulk  $\mu^{54}\text{Cr}$  composition is significantly more susceptible to this effect. Thus, considering the uncertainties involved in reconstituting the bulk composition, the calculated  $\mu^{54}\text{Cr}$  is also in agreement with that of the measured bulk Ivuna.

The stable isotope composition for the individual dissolution steps provides additional information previously not available (Fig. 5C). While the  $^{54}\text{Cr}$  data apparently suggest that the nucleosynthetic variability of  $^{54}\text{Cr}$  in the solar system is the result of variable contribution of a single carrier phase, the stable isotope data indicate that there are also large stable isotopic variations in the mineral assemblage of Ivuna. Although some of the variations are likely related to partial extraction and fractionation of Cr from a single carrier in different dissolution steps (e.g., steps L2-L5), the observation of reversing trends and individual peaks in the pattern of the dissolution experiment cannot be caused by a single and homogeneous Cr stable isotope composition. On the contrary, this observation suggest

that multiple carriers of Cr isotopes with diverse stable isotopic composition are present in Ivuna. Such presence of minerals with differences in their stable Cr isotope composition has the potential to explain the Cr stable isotope heterogeneity that exists between bulk solar system reservoirs<sup>40</sup>. In detail, carbonaceous chondrites are on average isotopically lighter than ordinary chondrites and Earth. The dissolution experiment reveals that some of the carriers of isotopically heavy Cr are mineralogically linked with the carriers of  $^{54}\text{Cr}$  enrichments (dissolution steps L8-L10). Although a direct correlation of Cr stable isotopic composition and variable  $^{54}\text{Cr}$  enrichment is not apparent from the meteorite data presented here, the presence of large stable isotopic variations in the step wise dissolution of Ivuna that appear to coexist with nucleosynthetic variability suggests that at least in part stable isotopic differences in bulk solar system reservoirs might be a result of the same process that imparted the nucleosynthetic variability in the same reservoirs.

## 4 Conclusions

In this paper we describe novel analytical protocols for the highly precise and accurate determination of the stable and mass-independent Cr isotopic composition of silicate samples by MC-ICPMS. Our results can be summarized as follows:

1. Repeat measurements of standards indicate that  $\mu^{53}\text{Cr}$  and  $\mu^{54}\text{Cr}$  can be measured with a precision that is better than 2.5 and 5.8, respectively. Although the method described here consumes substantially more Cr than traditional TIMS analyses, it also allows for a significantly improved (by a factor of at least two) reproducibility. The stable Cr isotope composition obtained concurrently to the mass-independent data has a precision of 0.05‰/Da, which is comparable to other studies.

## REFERENCES

## REFERENCES

2. Our high precision data reveals small differences in the mass-independent composition between different Cr standards and BSE when using the kinetic law for mass bias correction. These differences are best explained by loss of Cr during the production of the standards by equilibrium mass fractionation. This highlights the importance of carefully assessing and stating the Cr isotopic composition of the standard with respect to Earth when making precise measurements of the mass-independent composition.
3. When comparing data blocks equivalent to 1  $\mu\text{g}$  of Cr consumption a reproducibility of the MC-ICPMS data of 19 ppm for  $\mu^{54}\text{Cr}$  was achieved. This is comparable to the amount of Cr used by traditional TIMS analysis for similar precision, while the MC-ICPMS data also contains stable Cr isotope information and requires significantly less time allowing for increased sample throughput.
4. Stable Cr data for the achondrites Bilanga and NWA 2999 do not agree with the interpretation of Moynier et al.<sup>40</sup> that differences in the stable Cr isotope composition of Earth and chondrites are the result of fractionation during metal-silicate differentiation, but suggest, in agreement with the presence of mineralogical phases with distinct Cr stable isotopic composition in the CI chondrite Ivuna, that these differences are predominantly a result of slightly diverse Cr stable isotope compositions of the precursors they accreted from.
5. Step wise dissolution experiment of the CI chondrite Ivuna demonstrates the advantage of using the MC-ICPMS over the TIMS by revealing previously unknown carriers of large Cr stable isotope variations that co-vary with the known presence of carriers of large mass-independent anomalies.
- 3 R. Frei, C. Gaucher, S. W. Poulton and D. E. Canfield, *Nature*, 2009, **461**, 250–253.
- 4 D. Fibbi, S. Doumett, L. Lepri, L. Checchini, C. Gonnelli, E. Coppini and M. Del Bubba, *J. Hazard. Mater.*, 2012, **199**, 209–216.
- 5 G. Lugmair and A. Shukolyukov, *Geochim. Cosmochim. Acta*, 1998, **62**, 2863–2886.
- 6 A. Trinquier, J.-L. Birck and C. Allegre, *Astrophys. J.*, 2007, **655**, 1179–1185.
- 7 K. Yamashita, S. Maruyama, A. Yamakawa and E. Nakamura, *Astrophys. J. Lett.*, 2010, **723**, 20.
- 8 D. Hartmann, S. E. Woosley and M. F. El Eid, *Astrophys. J.*, 1985, **297**, 837–845.
- 9 B. S. Meyer, T. D. Krishnan and D. D. Clayton, *Astrophys. J.*, 1996, **462**, 825.
- 10 D. Clayton, *Handbook of Isotopes in the Cosmos: Hydrogen to Gallium*, Cambridge University Press, 2003, vol. 1.
- 11 N. Dauphas, L. Remusat, J. H. Chen, M. Roskosz, D. A. Papanastassiou, J. Stodolna, Y. Guan, C. Ma and J. M. Eiler, *Astrophys. J.*, 2010, **720**, 1577–1591.
- 12 L. Qin, L. R. Nittler, C. M. O. Alexander, J. Wang, F. J. Stadermann and R. W. Carlson, *Geochim. Cosmochim. Acta*, 2011, **75**, 629–644.
- 13 S. E. Woosley and A. Heger, *Rev. Mod. Phys.*, 2002, **74**, 1015–1071.
- 14 G. Wasserburg, M. Busso, R. Gallino and K. Nollett, *Nucl. Phys. A*, 2006, **777**, 5–69.
- 15 A. Trinquier, J.-L. Birck, C. J. Allègre, C. Gopel and D. Ulfbeck, *Geochim. Cosmochim. Acta*, 2008, **72**, 5146–5163.
- 16 F. Moynier, Q.-Z. Yin and B. Jacobsen, *Astrophys. J. Lett.*, 2007, **671**, L181–L183.
- 17 A. Trinquier, J.-L. Birck and C. J. Allegre, *J. Anal. At. Spectrom.*, 2008, **23**, 1565–1574.
- 18 L. Qin, C. M. O'D Alexander, R. W. Carlson, M. F. Horan and T. Yokoyama, *Geochim. Cosmochim. Acta*, 2010, **74**, 1122–1145.
- 19 A. Shukolyukov and G. Lugmair, *Geochim. Cosmochim. Acta*, 2004, **68**, 2875–2888.
- 20 A. Shukolyukov and G. W. Lugmair, *Earth Planet. Sci. Lett.*, 2006, **250**, 200–213.
- 21 R. Andreasen and M. Sharma, *Int. J. Mass Spectrom.*, 2009, **285**, 49–57.
- 22 M. Bizzarro, C. Paton, K. Larsen, M. Schiller, A. Trinquier and D. Ulfbeck, *J. Anal. At. Spectrom.*, 2011, **26**, 565–577.
- 23 K. K. Larsen, A. Trinquier, C. Paton, M. Schiller, D. Wielandt, M. A. Ivanova, J. N. Connelly, Å. Nordlund, A. N. Krot and M. Bizzarro, *Astrophys. J. Lett.*, 2011, **735**, L37.
- 24 M. Schiller, J. Baker, J. Creech, C. Paton, M.-A. Millet, A. Irving and M. Bizzarro, *Astrophys. J. Lett.*, 2011, **740**, L22.
- 25 M. Schiller, C. Paton and M. Bizzarro, *J. Anal. At. Spectrom.*, 2012, **27**, 38–49.

## 5 Acknowledgments

Funding for this project was provided by grants from the Danish National Research Foundation (grant number DNRF97) and from the European Research Council (ERC Consolidator grant agreement 616027-STARBUCK2ASTEROIDS) to M.B. We would also like to thank two anonymous reviewers for their thoughtful comments.

## References

- 1 M. Rotaru, J.-L. Birck and C. J. Allègre, *Nature*, 1992, **358**, 465–470.
- 2 A. S. Ellis, T. M. Johnson and T. D. Bullen, *Science*, 2002, **295**, 2060–2062.



## REFERENCES

## REFERENCES

- 1  
2  
3 26 M. B. Olsen, M. Schiller, A. N. Krot and M. Bizzarro, *Astrophys. J. Lett.*,  
4 2013, **776**, L1.  
5  
6 27 J. Foriel, F. Moynier, T. Schulz and C. Koeberl, *Meteorit. Planet. Sci.*,  
7 2013, 1–12.  
8 28 T. Inui, W. Abe, M. Kitano and T. Nakamura, *X Ray Spectrom.*, 2011, **40**,  
9 301–305.  
10 29 A. Pourmand and N. Dauphas, *Talanta*, 2010, **81**, 741–753.  
11 30 S. Weyer and J. B. Schwieter, *Int.. J. Mass Spectrom.*, 2003, **226**, 355–368.  
12 31 C. Paton, J. Hellstrom, B. Paul, J. Woodhead and J. Hergt, *J. Anal. At.*  
13 *Spectrom.*, 2011, **26**, 2508.  
14 32 W. R. Shields, T. J. Murphy, E. J. Catanzaro and E. L. Garner, *J. Res. Natl.*  
15 *Bur. Stand. A*, 1966, **70**, 193–197.  
16 33 K. Kehm, E. H. Hauri, C. M. O. Alexander and R. W. Carlson, *Geochim.*  
17 *Cosmochim. Acta*, 2003, **67**, 2879–2891.  
18 34 I. Platzner, J. V. Sala, F. Mousty, P. R. Trincherini and A. L. Poletini, *J.*  
19 *Anal. At. Spectrom.*, 1994, **9**, 719.  
20 35 I. Leya, M. Schönbächler, U. Wiechert, U. Krähenbühl and A. N. Halliday,  
21 *Int. J. Mass Spectrom.*, 2007, **262**, 247–255.  
22 36 H. Balsiger, J. Geiss and M. E. Lipschutz, *Earth Planet. Sci. Lett.*, 1969, **6**,  
23 117–122.  
24 37 P. Taylor, R. Maeck and P. De Bièvre, *Int.. J. Mass Spectrom.*, 1992, **121**,  
25 111–125.  
26 38 R. Schoenberg, S. Zink, M. Staubwasser and F. von Blanckenburg, *Chem.*  
27 *Geol.*, 2008, **249**, 294–306.  
28 39 L. Halicz, L. Yang, N. Teplyakov, A. Burg, R. Sturgeon and Y. Kolodny, *J.*  
29 *Anal. At. Spectrom.*, 2008, **23**, 1622.  
30 40 F. Moynier, Q.-Z. Yin and E. Schauble, *Science*, 2011, **331**, 1417–1420.  
31 41 M. Wadhwa, in *Rev. Mineral. Geochem.*, Mineral Soc America, 2008, pp.  
32 493–510.  
33 42 I. H. Campbell and H. St C O'Neill, *Nature*, 2012, **483**, 553–558.  
34 43 E. D. Young, A. Galy and H. Nagahara, *Geochim. Cosmochim. Acta*, 2002,  
35 **66**, 1095–1104.  
36 44 J.-L. Birck and C. J. Allègre, *Earth Planet. Sci. Lett.*, 1984, **11**, 943–946.  
37 45 A. Yamakawa, K. Yamashita, A. Makishima and E. Nakamura, *Astrophys.*  
38 *J.*, 2010, **720**, 150–154.  
39 46 K. Keil, *Chem. Erde - Geochem.*, 2012, **72**, 191–218.  
40 47 C. Paton, M. Schiller and M. Bizzarro, *Astrophys. J. Lett.*, 2013, **763**, L40.  
41  
42  
43  
44  
45  
46  
47  
48  
49  
50  
51  
52  
53  
54  
55  
56  
57  
58  
59  
60