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Stable chromium isotopic composition of meteorites and metal–silicate experiments: Implications for fractionation during core formation

P. Bonnand ^{a,*}, H.M. Williams ^b, I.J. Parkinson ^{c,d}, B.J. Wood ^a, A.N. Halliday ^a^a Department of Earth Sciences, University of Oxford, South Parks Road, Oxford, OX1 3AN, United Kingdom^b Department of Earth Sciences, Durham University, Sciences Labs, Durham, DH1 3LE, United Kingdom^c School of Earth Sciences, University of Bristol, Bristol, BS8 1RJ, United Kingdom^d Department of Environment, Earth and Ecosystems, CEP SAR, The Open University, Walton Hall, Milton Keynes, MK7 6AA, United Kingdom

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ABSTRACT

We present new mass independent and mass dependent Cr isotope compositions for meteorites measured by double spike thermal ionisation mass spectrometry. Small differences in both mass independent ^{53}Cr and ^{54}Cr relative to the Bulk Silicate Earth are reported and are very similar to previously published values. Carbonaceous chondrites are characterised by an excess in ^{54}Cr compared to ordinary and enstatite chondrites which make mass independent Cr isotopes a useful tool for distinguishing between meteoritic groups. Mass dependent stable Cr isotope compositions for the same samples are also reported. Carbonaceous and ordinary chondrites are identical within uncertainty with average $\delta^{53}\text{Cr}$ values of $-0.118 \pm 0.040\text{‰}$ and $-0.143 \pm 0.074\text{‰}$ respectively. The heaviest isotope compositions are recorded by an enstatite chondrite and a CO carbonaceous chondrite, both of which have relatively reduced chemical compositions implying some stable Cr isotope fractionation related to redox processes in the circumstellar disk. The average $\delta^{53}\text{Cr}$ values for chondrites are within error of the estimate for the Bulk Silicate Earth (BSE) also determined by double spiking. The lack of isotopic difference between chondritic material and the BSE provides evidence that Cr isotopes were not fractionated during core formation on Earth. A series of high-pressure experiments was also carried out to investigate stable Cr isotope fractionation between metal and silicate and no demonstrable fractionation was observed, consistent with our meteorites data. Mass dependent Cr isotope data for achondrites suggest that Cr isotopes are fractionated during magmatic differentiation and therefore further work is required to constrain the Cr isotopic compositions of the mantles of Vesta and Mars.

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1. Introduction

Variations in chemical composition in the Solar System reflect early nebular processes as well as planetary accretion and differentiation. Metal–silicate differentiation (or core formation) is a particularly dramatic process that transforms the budgets of slightly-to strongly-siderophile elements in the residual bulk silicate Earth (BSE). These chemical changes in the Earth have been replicated experimentally and modelled over many years, as reviewed elsewhere (e.g. Newsom, 1990; Wood et al., 2008). During Earth accretion and core formation, the elements were distributed between the mantle (silicate phases) and the core (Fe-rich phases) according to their bulk distribution coefficients ($D = X_{\text{metal}}/X_{\text{silicate}}$). Vari-

ably siderophile ($D > 0$) as opposed to strictly lithophile ($D = 0$) elements are respectively depleted and enriched (by removal of metal) in the mantle. Non-chondritic elemental ratios in the residual terrestrial mantle, such as Mg/Si, have been used to argue that light elements like Si became slightly siderophile ($D > 0$) and were incorporated into the Earth's core (Allègre et al., 1995; Drake and Righter, 2002). A new tool to assess the removal of elements into the core is to utilise the fractionation of stable isotopes between metal and silicate, which also provide insights into the reactions occurring during core formation and constraints on key physical parameters such as temperature, pressure and oxygen fugacity. Such mass dependent isotopic variations have already been utilised in this way for Si (Georg et al., 2007; Armytage et al., 2011; Zambardi et al., 2013), Fe (Williams et al., 2012) and Cr (Moynier et al., 2011).

Stable isotopes can be fractionated between phases by both kinetic processes and equilibrium fractionation processes. In the latter case, the fractionation is dependent on speciation, coordination

* Corresponding author. Present address: Department of Earth Sciences, University of Oxford, South Parks Road, Oxford, OX1 3AN, United Kingdom. Tel.: +44 (0)1865 272044; fax: +44 (0)1865 272072.

E-mail address: pierre.bonnand@earth.ox.ac.uk (P. Bonnand).

and bonding environment, where the isotopically heavier species are generally associated with a lower coordination and higher oxidation states of the element of interest (Schauble, 2004). It has been proposed that metal–silicate equilibrium could lead to an isotopic shift due to the difference in bonding between metal and silicate liquids (Georg et al., 2007). If the metal fraction is enriched or depleted relative to the silicate fraction then the bulk silicate Earth (BSE) should be isotopically fractionated relative to the starting material (bulk undifferentiated chondrites). Therefore stable isotopes of variably siderophile elements have great potential to better constrain core formation processes (Georg et al., 2007). Laboratory experiments have been performed to replicate and understand mass dependent fractionation between metal and silicate melts (Hin et al., 2013; Shahar et al., 2011). However, the isotopic fractionations at high temperature are small and high precision measurements are needed to resolve these variations.

Chromium is an element of great interest to core formation because it becomes more siderophile under more reducing conditions (iron-wüstite (IW) -1.5 to -5 log units) and at high temperatures (1480 to 2000 °C) with a D value of 2.5–3.5 (Wood et al., 2008), but is less sensitive to pressure effects. It has been argued that ~60% of the Earth's total Cr is in the core such that the mantle is depleted in Cr relative to chondrites (Allègre et al., 1995; McDonough, 2003). Therefore it is possible that during core formation stable Cr isotopes are fractionated. Indeed, it has previously been proposed that the Cr isotopic composition of the BSE is fractionated by metal–silicate fractionation relative to chondrites with the stable Cr isotopic composition of meteorites reported to be lighter than the BSE value (Moynier et al., 2011). The same study presented ab-initio calculations that demonstrated that the metal fraction should be isotopically enriched in ^{52}Cr (that is lighter) compared to the silicate phase, in agreement with their interpretation of Cr isotope fractionation during core formation (Moynier et al., 2011).

Earlier studies of Cr isotopes in meteorites have focussed on radiogenic ($\varepsilon^{53}\text{Cr}$) and nucleosynthetic ($\varepsilon^{54}\text{Cr}$) variations (e.g. Birck and Allègre, 1988; Shukolyukov and Lugmair, 2006; Trinquier et al., 2007, 2008a; Moynier et al., 2007; Qin et al., 2010). Variations in $\varepsilon^{53}\text{Cr}$ are due to the decay of ^{53}Mn (half-life 3.7 Ma) and are related to the Mn/Cr ratio and time, whereas variations in $\varepsilon^{54}\text{Cr}$ are due to the production of this neutron rich isotope in a type 1a supernova (e.g. Hartmann et al., 1985). It is also possible that Cr isotopes are influenced by spallation reactions during cosmic ray exposure (Leya et al., 2003). However, spallation effects are believed to be negligible for samples with low Fe/Cr, including the samples we discuss in this paper.

While variations in radiogenic and nucleosynthetic Cr isotopes are not directly relevant to core formation these studies have utilised high precision thermal ionisation mass spectrometry (TIMS) techniques that allow assessment of variations in $\varepsilon^{53}\text{Cr}$ and $\varepsilon^{54}\text{Cr}$ at the 10 ppm (0.1‰ unit) level (e.g. Trinquier et al., 2008b). By contrast, mass dependent Cr isotopes have the potential to characterise Cr behaviour during core formation on Earth and other planetary bodies, but studies have used less precise multi-collector inductively-coupled-plasma mass spectrometry (MC-ICP-MS) techniques with precisions of ~50 ppm (Schoenberg et al., 2008; Moynier et al., 2011; Schiller et al., 2014). The composition of the BSE has been determined by several studies using the double-spike technique yielding a $\delta^{53}\text{Cr} -0.12 \pm 0.10\text{‰}$ (Fig. 1, Schoenberg et al., 2008; Farkaš et al., 2013). This relatively uniform value indicates that magmatic processes do not significantly fractionate stable Cr isotopes, although data for lunar samples indicates extensive magmatic differentiation can produce $\delta^{53}\text{Cr}$ compositions ~0.1‰ lighter than the lunar and terrestrial mantle (Fig. 1, Bonnand et al., in press). By contrast, Moynier et al. (2011) and Schiller et al. (2014) use a standard-sample bracketing technique and re-

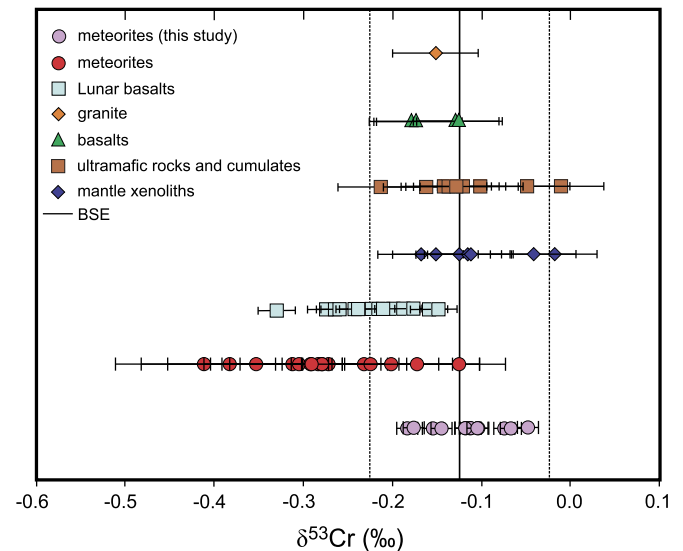


Fig. 1. Compilation of Cr data in high temperature rocks. The granite, basalts and ultramafic rocks and cumulates data are from Schoenberg et al. (2008), the meteorite data is from Moynier et al. (2011), Schiller et al. (2014) and this study. The lunar samples data is from Bonnand et al. (in press). The thick vertical line represents the mean and the thin vertical lines ± 2 s.d. of the terrestrial data from Schoenberg et al. (2008).

port significant isotopic difference in $\delta^{53}\text{Cr}$ between chondritic meteorites and the BSE, with the meteorites being 0.3‰ lighter. However, a recent study by Qin et al. (2015) using the double-spike technique reveals no such difference. Clearly a resolution of these differences is required.

Here we utilise high-precision TIMS measurements and the double-spike technique to extend the high precision Cr isotope meteorite dataset. These data provide assessment of both the mass independent and mass dependent variations in meteorites. We also investigate the Cr isotope fractionation between metal and silicate phases in high pressure experiments. The data are compared to published datasets and discrepancies between the different studies are discussed. We then attempt to understand the origins of Cr isotope variations in the meteorite dataset and discuss the use of Cr isotopes to study core formation processes.

2. Samples

We have determined the Cr-isotope compositions of 19 meteorites. Meteorite samples include four carbonaceous chondrites (Allende (CV3), Orgueil (CI), Murchison (CM2) and Ornans (CO3)), six ordinary chondrites (Bremervörde (H/L3), Kernouvé (H6), Barratta (L4), Bruderheim (L6), Parnallee (LL3) and Saint-Séverin (LL6)), two enstatite chondrites (Indarch (EH4) and Khaipur (EL6)), one martian meteorites (Nakhla) and four HED meteorites (Kapoeta (howardite), Pasamonte (eucrite), Juvinas (eucrite) and Johnstown (diogenite)). We also present data for a terrestrial peridotite (JP-1). Five experimental isotope equilibrium runs have been performed and for each run, metal and silicate have been analysed (Table 1).

3. Analytical methods

3.1. Metal–silicate experiments

The experiments designed to study Cr isotopic fractionation between metal and silicate were similar to those used for Zn (Bridgestock et al., 2014). Briefly, the starting materials were prepared from high purity oxide (70%) and metal (30%) powders. The silicate starting material approximates the 1.5 GPa eutectic composition in the system anorthite–diopside–forsterite ($\text{An}_{50}\text{Di}_{28}\text{Fo}_{22}$,

Table 1
Chromium concentration and Cr isotopic composition for metal and silicate fraction for the five experiments performed in this study. The Cr concentrations were analysed by ICP-MS at the University of Oxford. The 2 s.d. for $\delta^{53}\text{Cr}$ is the external reproducibility on the JP-1 measurement (see text for details, Bonnand et al., in press).

Sample name	Capsule	Run time (min)	Fraction	Cr ($\mu\text{g g}^{-1}$)	$D_{\text{met-silicate}}$	$\delta^{53}\text{Cr}$	2 s.d.	$\Delta^{53}\text{Cr}$	2 s.d.			
A171	Si	70	metal	8723	1.02	-0.166	0.022	0.010	0.031			
			silicate	8584		-0.175						
A176	Mg	10	metal	11880	1.18	-0.132	0.022	-0.008	0.031			
			silicate	10082		-0.124						
B100	Mg	40	metal	13658	2.00	-0.039	0.022	0.045	0.031			
			metal (rep)			-0.024				0.022	0.060	0.031
			silicate	6836		-0.084				0.022		
B97	Si	43	metal	5872	0.87	-0.195	0.022	-0.024	0.031			
			silicate	6788		-0.170						
B98	Si	10	metal	8165	0.97	-0.245	0.022	-0.008	0.031			
			silicate	8398		-0.237						

Presnall et al., 1978) and was doped with 2 wt.% Cr (as Cr_2O_3). Experiments were carried out in either polycrystalline MgO or silica glass capsules with graphite furnaces. The experiments were performed at 1.5 GPa in a piston cylinder apparatus at the Department of Earth Sciences, University of Oxford. In order to ensure complete melting of both metal and silicate, the run temperature was 1650 °C and was monitored using W_{95}Re_5 – $\text{W}_{74}\text{Re}_{26}$ thermocouples. Experimental run times varied from 10 to 70 min (Table 1). The experiments were quenched by turning off the power, after which the pressure was slowly released. After quenching, the charges were lightly hand-crushed and the two phases were hand-picked under a binocular microscope.

3.2. Sample preparation for meteorites

In order to obtain accurate mass dependent, each sample was analysed for its radiogenic and nucleosynthetic Cr isotope compositions and an aliquot of the same solution was spiked and analysed for its mass dependent Cr isotopic composition. Spiking occurred before any separation chemistry and the unspiked and spiked samples were processed in the same way. Protocols for the separation of Cr from geological and environmental samples have been previously described (e.g. Ball and Izbicki, 2004; Trinquier et al., 2008b; Bonnand et al., 2011, 2013, in press; Schiller et al., 2014). A summary of the method used in this study is given below.

For silicate samples, approximately 20 mg of whole rock powder were digested using concentrated HNO_3 –HF–HCl acid mixtures. The fully dissolved sample was evaporated to dryness and then dissolved in 6 M HCl. Two aliquots of $\sim 2 \mu\text{g}$ of chromium was dried and dissolved in 6 M HCl and one of them was spiked with the requisite amount of double spike (^{50}Cr – ^{54}Cr). Chromium separation from silicate matrices requires two columns. The first separates Cr from the main matrix cations (e.g. Ca, Na, Mg) and a full description is given in Bonnand et al. (2011). For the purposes of this study, a disposable Bio-Rad Poly-Prep 10 ml column was filled with 1 ml of AG50 X8 (200–400 mesh chloride form resin) and the sample was loaded and eluted in 0.5 M HCl. The Cr fraction and small quantities of other minor elements such as Ti pass straight through this column and were collected during this first elution. In order to clean the Cr fraction from isobaric interferences (Ti, V and Fe) a second column chemistry was performed. The Cr fraction was dried and dissolved in 0.5 M HNO_3 . A disposable Bio-Rad Poly-Prep column was filled with 1 mL of AG50 X8 200–400 mesh resin. The resin was first cleaned with 20 ml 6 M HCl and 20 mL MQ H_2O and then preconditioned with 10 mL of 0.5 M HNO_3 . The sample was then loaded in 4 mL 0.5 M HNO_3 . In a weak HNO_3 medium, Cr(III) will stick to the cation resin. The column is then washed with 4 mL 0.5 M HNO_3 , then 6 mL 0.5 M HNO_3 + 0.25 M HF, then 7 mL 0.5 M HCl. Finally, the cleaned Cr fraction is eluted with 6 mL 3 M HCl. The second step of the separation protocol

has a yield better than 96%, although the total procedure yield for the two separations is about 80%. The total blank of this chemical process is ~ 0.2 ng, which is negligible compared to the 2000 ng processed through the columns.

The protocol used for the separation of the Cr fraction from Fe rich samples is different, involving three columns. The first column is designed to remove Fe from the sample and has been described in Bonnand et al. (2013). To this end, a disposable Bio-rad Poly-Prep 10 ml column was filled with 1 ml of AG1 X8 and the sample loaded in 7 M HCl. The Fe sticks to the column whereas Cr is eluted. After this first column the samples are treated in the same way as silicate samples.

3.3. Mass spectrometry

The chromium isotope analyses of the meteorite samples were performed with a ThermoFisher Triton Thermal Ionisation Mass Spectrometer (TIMS) in static multicollection mode at the University of Oxford (UK). Chromium samples were loaded onto an outgassed zone refined Re filament in 1 μL 6 M HCl, along with 3 μL of a mixture of silicic and boric acids. The filament was slowly heated at 0.65 A to dry down the sample. The current was then increased until a dull red glow was observed. Amplifier gains were performed daily and the baseline was measured after each block of 10 cycles, with amplifier rotation after each block. Samples and standards were run in static mode with a typical beam current of $6\text{--}8 \times 10^{-11}$ A of ^{52}Cr for 54 blocks of 10 cycles (with an integration time per cycle of 8.4 s). Interferences were monitored on ^{56}Fe , ^{49}Ti and ^{51}V , such that ^{54}Cr (^{56}Fe) and ^{50}Cr (^{50}Ti and ^{50}V) signals were corrected for isobaric interferences. These corrections were always negligible. For un-spiked runs, Cr isotope ratios were corrected for mass fractionation using an exponential law and $^{50}\text{Cr}/^{52}\text{Cr} = 0.051859$ (Shields et al., 1966) (see Section 3.4).

The external reproducibility and accuracy of $\varepsilon^{53}\text{Cr}$ and $\varepsilon^{54}\text{Cr}$ were assessed by 2 standard deviation of NIST SRM 979 processed through chemical purification and is 0.00 ± 0.10 and 0.00 ± 0.19 respectively (2 s.d., $n = 15$, Table 2). The accuracy of the mass dependent variation ($\delta^{53}\text{Cr}$) was assessed by repeat measurements of a NIST SRM 979 Cr standard and is $-0.005 \pm 0.009\text{‰}$ (2 s.d., $n = 15$, Table 2). The external reproducibility was assessed with repeated measurements of Orgueil sample and is $-0.145 \pm 0.012\text{‰}$ (2 s.d., $n = 6$, Table 2). This is at least a four times improvement compared to previous studies (Moynier et al., 2011). The uncertainties associated with the individual $\delta^{53}\text{Cr}$ data reported in Table 2 incorporate errors propagated from the unspiked and spiked analyses.

Chromium stable isotope analyses of the experimental samples were performed with a ThermoFisher Neptune Multi collector ICP-MS at the Open University. The analytical protocols have been previously described (Bonnand et al., 2011, in press). The

Table 2

Mass independent and mass dependent Cr isotopic compositions for meteorites and terrestrial samples analysed in this study. The Cr concentrations are from Qin et al. (2010), Trinquier et al. (2008a) and Shukolyukov and Lugmair (2006).

Sample name	Group	Cr ($\mu\text{g g}^{-1}$)	$\varepsilon^{53}\text{Cr}$	$2\sigma^a$	$\varepsilon^{54}\text{Cr}$	$2\sigma^a$	n^b	$\delta^{53}\text{Cr}$ (‰)	$2\sigma^c$	n^d
NIST SRM979		n/a	0.00	0.10	0.00	0.19	15	0.000	0.009*	15
JP-1		2780	0.11	0.10	0.28	0.19	3	-0.102	0.012	5
<i>Carb. Chondrite</i>										
Allende	CV3	3600	0.14	0.10	1.04	0.19	1	-0.113	0.012	4
Orgueil	CI	2650	0.53	0.10	1.45	0.19	6	-0.145	0.012	6
Murchison	CM2	3100	0.36	0.10	0.98	0.19	1	-0.119	0.012	1
Ornans	CO3	3300	0.19	0.10	1.03	0.19	1	-0.068	0.012	1
Average CC								-0.111	0.065	
<i>Ord. Chondrite</i>										
Bremervörde	H/L3	3600	0.36	0.10	0.36	0.19	1	-0.146	0.012	1
Kernouve	H6	3700	0.27	0.10	0.27	0.19	1	-0.111	0.012	1
Barratta	L4	3740	0.29	0.10	-0.10	0.19	1	-0.118	0.012	1
Bruderheim	L6	3400	0.30	0.10	-0.26	0.19	1	-0.112	0.012	1
Parnallee	LL3	3200	0.38	0.10	-0.08	0.19	1	-0.117	0.012	1
Saint-Severin	LL6	3970	0.38	0.10	0.38	0.19	1	-0.104	0.012	1
Average OC								-0.118	0.029	
<i>Enst. Chondrite</i>										
Indarch	EH4	3400	0.37	0.10	0.15	0.19	1	-0.103	0.012	1
Khairpur	EL6	4060	0.27	0.10	0.14	0.19	1	-0.048	0.012	1
Average EC								-0.076	0.078	
<i>HED</i>										
Kapoeta	How.	3600	0.32	0.10	-0.71	0.19	1	-0.156	0.012	1
Pasamonte	Eucrite	1750	1.03	0.10	-0.45	0.19	1	-0.176	0.012	1
Juvinas	Eucrite	2100	0.93	0.10	-0.55	0.19	1	-0.184	0.012	1
Johnstown	Diog.	5700	0.32	0.10	-0.56	0.19	1	-0.074	0.012	1
<i>Mars</i>										
Nakhla	SNC	1770	0.27	0.10	-0.35	0.19	1	-0.156	0.012	1

Note: Carb.: carbonaceous, Ord.: ordinary, Enst.: enstatite, How.: howardite, Diog.: diogenite.

^a 2 standard deviations of repeated measurements of the NIST 979 standard.

^b Number of unspiked runs.

^c 2 standard deviations of repeated measurements of Orgueil sample.

^d Number of spiked runs.

* 2 standard deviations of the NIST 979 (see text for details).

external reproducibility obtained on this instrument was assessed with replicate measurements of JP-1 standard and yield a value of $-0.128 \pm 0.022\text{‰}$ (2 s.d., $n = 14$, Bonnand et al., in press).

3.4. Deconvolution procedure

We need to correct for mass fractionation that occurs during chemical separation and mass spectrometry analyses. To do this we employ two methodologies to deconvolve the isotope data in this paper, and the rationale for this is as follows. For terrestrial samples, there is no variation in mass independent ^{53}Cr and ^{54}Cr (e.g., Trinquier et al., 2008a; Qin et al., 2010) and therefore all samples (including NIST SRM 979) lie on a single mass fractionation trend in four isotope space, so that only a double-spiked analyses is required to derive the stable isotope composition of Cr isotopes (e.g. Schoenberg et al., 2008; Bonnand et al., 2011). The metal-silicate experiments samples were deconvolved in this way using the NIST SRM 979 standard value as the natural composition as in previous studies for terrestrial samples (e.g. Schoenberg et al., 2008).

For extra-terrestrial samples this assumption is not true as there are resolvable variations in mass independent Cr isotopes, such that samples do not lie on a single mass fractionation trend. Therefore for meteoritic samples the unspiked runs were first internally normalised using an exponential law to the canonical $^{50}\text{Cr}/^{52}\text{Cr}$ ratio of 0.051859 (Shields et al., 1966) to reveal any mass independent $\varepsilon^{53}\text{Cr}$ and $\varepsilon^{54}\text{Cr}$ variation. By definition this removes any mass dependent information but provides data comparable to other studies (Birck and Allègre, 1988; Shukolyukov and Lugmair, 2006; Moynier et al., 2007; Trinquier et al., 2007, 2008a; Yin et al.,

2007; Qin et al., 2010). Finally the unspiked run is also combined with the spiked run for each sample in the double spike calculation and allows the determination of the mass dependent Cr stable isotope composition (and the true isotope composition in four isotope space).

4. Results

Seventeen meteorite samples were analysed. All data are reported in Table 2. Radiogenic and nucleosynthetic variations are reported using the equation:

$$\varepsilon^X\text{Cr} = \left(X\text{Cr}/^{52}\text{Cr}_{\text{sample}} / X\text{Cr}/^{52}\text{Cr}_{\text{SRM979}} - 1 \right) \times 10\,000$$

where $X\text{Cr}/^{52}\text{Cr}_{\text{sample}}$ is the mass fractionation corrected isotope ratios ($X\text{Cr}$ is either ^{53}Cr or ^{54}Cr). The mass dependent variations are reported using the equation below:

$$\delta^{53}\text{Cr} = \left(^{53}\text{Cr}/^{52}\text{Cr}_{\text{sample}} / ^{53}\text{Cr}/^{52}\text{Cr}_{\text{SRM979}} - 1 \right) \times 1000$$

where the ratio $^{53}\text{Cr}/^{52}\text{Cr}_{\text{sample}}$ is the ratio obtained after the double spike deconvolution procedure and is corrected for mass dependent fractionation occurring during sample preparation and mass spectrometry. The $^{53}\text{Cr}/^{52}\text{Cr}$ and $^{54}\text{Cr}/^{52}\text{Cr}$ isotopic ratios for the SRM 979 standard used in this study for normalisation are 0.1134563 and 0.0282115 respectively.

Internally normalised isotope ratios ($^{53}\text{Cr}/^{52}\text{Cr}$ and $^{54}\text{Cr}/^{52}\text{Cr}$) for the NIST SRM 979 standards are not correlated and this indicates that a double normalisation using $^{54}\text{Cr}/^{52}\text{Cr}$ ratio is not necessary to correct for mass isotope fractionation (i.e. there is

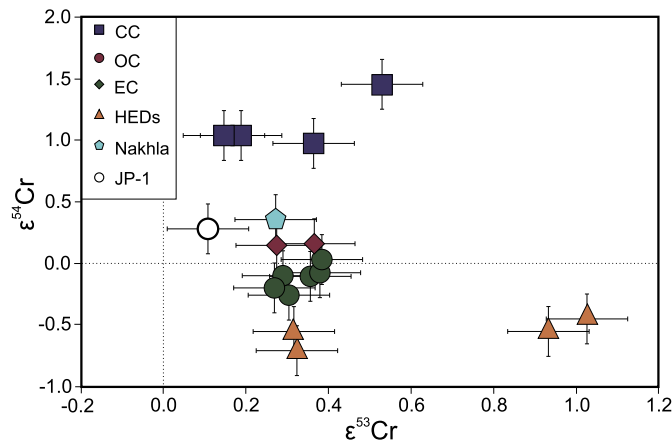


Fig. 2. Mass independent chromium isotopic compositions for bulk meteorites analysed in this study. CC: carbonaceous chondrites, OC: ordinary chondrites, EC: enstatite chondrites, HED: howardite-eucrite-diogenite.

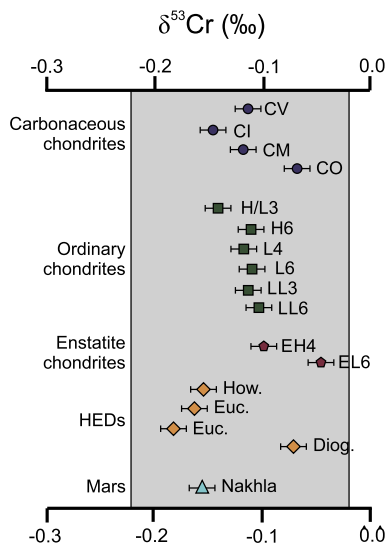


Fig. 3. Stable Cr isotopic compositions in meteorites analysed in this study. The grey vertical bar is the current estimate (mean \pm 2 s.d.) for the Bulk Silicate Earth (BSE) from Schoenberg et al. (2008).

no residual mass fractionation variation in the data at the level of analytical uncertainty). Radiogenic $\epsilon^{53}\text{Cr}$ values for meteorites analysed in this study range from 0.14 to 1.03 and nucleosynthetic $\epsilon^{54}\text{Cr}$ values between -0.71 and 1.45 . Carbonaceous chondrites show excess ^{54}Cr compared to ordinary chondrites (Fig. 2). There is no clear relationship between $\epsilon^{53}\text{Cr}$ and $\epsilon^{54}\text{Cr}$ (Fig. 2), however. Overall, the data obtained in this study are in agreement with previously published data for non-mass dependent Cr isotope variations in meteorites (Trinquier et al., 2007, 2008a; Qin et al., 2010) when the offset due to normalisation is taken into account.

For mass dependent fractionation the samples analysed in this study are characterised by $\delta^{53}\text{Cr}$ values ranging from -0.184 to -0.048‰ . The data are presented in Table 2 and Fig. 3. The carbonaceous chondrites have an average $\delta^{53}\text{Cr}$ value of $-0.111 \pm 0.065\text{‰}$ ($n = 4$) and display some variations with the CO sample having the heaviest $\delta^{53}\text{Cr}$ values. The ordinary chondrites are characterised by very little spread in $\delta^{53}\text{Cr}$ values with a mean $\delta^{53}\text{Cr}$ value of $-0.118 \pm 0.029\text{‰}$ ($n = 6$). Enstatite chondrites display greater spread in $\delta^{53}\text{Cr}$ but only two samples have been measured with Khaipur being the heaviest sample in this study ($\delta^{53}\text{Cr} = -0.048\text{‰}$). Finally, HED and martian meteorites have $\delta^{53}\text{Cr}$ values ranging from -0.166 to -0.070‰ .

The results for five metal-silicate experiments are presented in Table 1. Overall, metal and silicate pairs from the five experiments have slightly different Cr stable isotope compositions. However, the Cr isotopic composition of the metal and the silicate fractions are in all cases identical or barely distinguishable; B100 has $\Delta^{53}\text{Cr}$ ($\Delta^{53}\text{Cr} = \delta^{53}\text{Cr}_{\text{metal}} - \delta^{53}\text{Cr}_{\text{silicate}}$) of 0.045 ± 0.031 (Table 1). There is a good correlation between the Cr stable isotope compositions of the metal and silicate pairs and experimental run duration for both Mg and Si capsule experiments (Fig. 4).

5. Discussion

In this section we first discuss mass independent variations in Cr isotopes. We then estimate the mass dependent fractionation during metal segregation and discuss the implication for the utility of stable Cr isotopes to study core formation on Earth. Finally, we discuss the potential explanations for mass dependent variations in the meteorite dataset relative to other published meteorite datasets.

5.1. Variation in $\epsilon^{53}\text{Cr}$ and $\epsilon^{54}\text{Cr}$

The meteorites analysed in this study display significant variations in both $\epsilon^{53}\text{Cr}$ and $\epsilon^{54}\text{Cr}$. All chondrites show either a weak positive or no anomaly in $\epsilon^{53}\text{Cr}$ compare to terrestrial samples and this is due to variations in the Mn/Cr ratio in primordial materials. In the literature, Orgueil and Allende samples show small excesses in $\epsilon^{53}\text{Cr}$ and have been used to estimate timescales for the formation of the Earth (Shukolyukov and Lugmair, 2006; Trinquier et al., 2008a; Moynier et al., 2007; Qin et al., 2010). Given the relatively small isotopic variations reported in this study and the reproducibility of our measurements, we have not attempted to use our carbonaceous chondrites data to reconstruct a unique initial $^{53}\text{Mn}/^{55}\text{Mn}$ ratio of the solar system. Ordinary chondrites display a smaller spread in their $\epsilon^{53}\text{Cr}$ values.

The HED achondrites are characterised by large $\epsilon^{53}\text{Cr}$ variations and this suggests that differentiation of Vesta was extremely rapid. With a half-life of 3.7 Ma for ^{53}Mn and the differences between the HED meteorites can only reasonably be explained by early fractionation of the Mn/Cr ratios during Vesta's differentiation. To be recorded by the $^{53}\text{Mn}/^{53}\text{Cr}$ system, the differentiation must have happened in the first 20 Ma of the asteroid history. This is in agreement with previously published data on eucrite parent body (Trinquier et al., 2008a).

Among all chondrite groups, carbonaceous chondrites show the largest ^{54}Cr anomalies with values ranging from 0.98 to 1.45. The two enstatite chondrites analysed show similar ^{54}Cr excesses to those of carbonaceous chondrites. Finally, ordinary chondrites show a small spread in $\epsilon^{54}\text{Cr}$ values but are depleted in ^{54}Cr relative to other chondrites and terrestrial samples. It was previously proposed (e.g. Qin et al., 2010) that variations in $\epsilon^{54}\text{Cr}$ could be used to identify meteorite groups or parent bodies and the data presented in this study agree with this interpretation.

5.2. Isotope fractionation during metal-silicate partitioning

Two experiments of 10 min and 40 min duration were performed in MgO capsules and three further experiments of 10 min, 45 min and 70 min duration were carried out in silica capsules (Table 1). The experimental products were analysed for their Cr concentration and isotopic compositions in order to calculate Cr metal-silicate distribution coefficients ($D_{\text{met-sil}} = [\text{Cr}]_{\text{met}}/[\text{Cr}]_{\text{silicate}}$) and stable isotope fractionation factors $\Delta^{53}\text{Cr}_{\text{met-sil}} = \delta^{53}\text{Cr}_{\text{met}} - \delta^{53}\text{Cr}_{\text{sil}}$ (Table 1).

The $D_{\text{met-silicate}}$ values for the silica capsules experiments are very consistent at 0.87 to 1.02 (Table 1), in agreement with results from previous high-pressure experimental studies

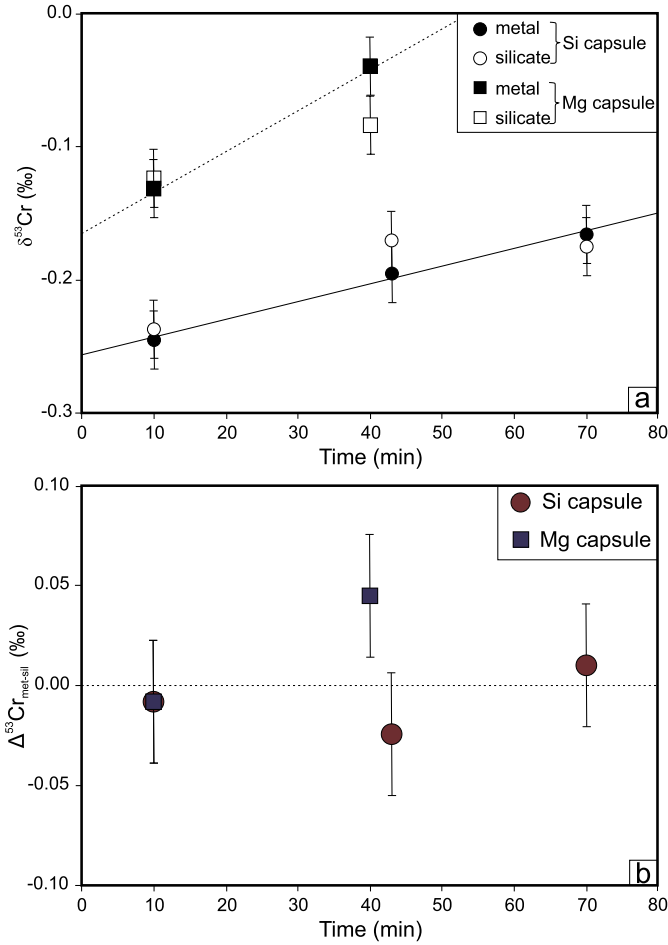


Fig. 4. (a) Chromium isotopic compositions of metal–silicate experiments versus time. The solid and dashed lines track the Cr isotopic evolution of the phases through time in the silica (Si) and magnesium (Mg) capsules respectively. (b) Fractionation factors ($\Delta^{53}\text{Cr}_{\text{met-sil}} = \delta^{53}\text{Cr}_{\text{metal}} - \delta^{53}\text{Cr}_{\text{silicate}}$) versus time for the five experiments analysed in this study. The dashed line is $\Delta^{53}\text{Cr}_{\text{met-sil}} = 0$.

(Tuff et al., 2011). The two experiments in MgO capsules have slightly different $D_{\text{met-silicate}}$, of 1.18 (A176) and 2.00 (B100) which might reflect small differences in oxygen fugacity between them. The silicate fraction of experiment B100 was, however, extremely difficult to separate from the capsule and it is likely that the silicate fraction of this sample has been contaminated to some extent by capsule material. This is the likeliest explanation for the lower Cr concentration obtained in the silicate fraction and the higher apparent $D_{\text{met-silicate}}$ of this experiment. Therefore, experiment B100 should not be used to assess whether isotope fractionation occurred during metal–silicate partitioning. The consistency of the $D_{\text{met-silicate}}$ values obtained for experiment durations ranging from 10 min to 70 min provides strong evidence for the attainment of Cr equilibrium between metal and silicate during the experiments. This is also consistent with earlier observations on equilibrium times for metal–silicate partitioning (Tuff et al., 2011; Wood and Halliday, 2010).

In terms of Cr isotope partitioning, the metal and silicate phases in all experimental products have very similar Cr stable isotope compositions. The Cr isotopes compositions of both metal and silicate phases in all experiments show a correlation with experiment duration (Fig. 4), both metal and silicate phases becoming increasingly heavy with time. This can be interpreted in terms of loss of isotopically light Cr to the capsule. The metal and silicate phases from MgO capsule experiments have heavier $\delta^{53}\text{Cr}$ values than those from silica capsules (Fig. 4). This is probably due the greater

tendency of crystalline MgO to dissolve Cr, facilitating loss of Cr to the capsule walls. These observations are in agreement with previous experimental studies (Tuff et al., 2011), which demonstrated that Cr is indeed lost to the capsule but that this loss is relatively small. The co-evolution of both silicate and metal Cr isotopic compositions with time provides further evidence for attainment of Cr equilibrium between metal and silicate during the experiments.

The Cr metal–silicate isotope fractionation $\Delta^{53}\text{Cr}_{\text{met-sil}}$ in the silica capsule experiments ranges from $-0.024 \pm 0.031\text{‰}$ (43 min) to $+0.010 \pm 0.031\text{‰}$ (70 min) and in the MgO capsule experiment $\Delta^{53}\text{Cr}_{\text{met-sil}}$ is $-0.008 \pm 0.031\text{‰}$ (10 min). The time series experiments conducted in silica capsules show no observable correlation between metal–silicate fractionation and experiments duration (Fig. 4). Therefore, although some Cr is lost to the capsule, the metal and silicate phases appear to have reached equilibrium before this point, and they remain at equilibrium during the experiment, even as minor Cr is lost to the capsule. Importantly, in all of the experiments $\Delta^{53}\text{Cr}_{\text{met-sil}}$ is within uncertainty of zero indicating negligible Cr isotope fractionation between molten metal and silicate.

The experiments carried out for this study were performed at 1.5 GPa and 1650 °C which correspond to a depth of about 45 km on Earth. Metal segregation and core formation on Earth undoubtedly happened at considerably higher pressure and temperature (Wade and Wood, 2005). Although the effect of pressure is unknown, the increase of temperature will have an impact on the isotope fractionation (as $1/T^2$), such that the magnitude of $\Delta^{53}\text{Cr}_{\text{met-sil}}$ should decrease. Given our results therefore, it is unlikely that metal segregation at higher pressure and temperature is associated with any isotope fractionation. We conclude that there is no evidence of significant Cr isotope fractionation during metal–silicate partitioning on Earth but that further experiments under conditions more closely approximating those of core formation would enable more stringent testing of this conclusion.

5.3. Mass dependent chromium isotopic fractionation in meteorites

The chondrites analysed in this study are characterised by double-spike derived $\delta^{53}\text{Cr}$ values ranging from $-0.146 \pm 0.012\text{‰}$ to $-0.048 \pm 0.012\text{‰}$ (Fig. 5). Although the total range of fractionation is small, it is three times larger than previously reported for radiogenic variations indicating that mass dependent processes dominate the variation. The data reported for chondrites are not in agreement with previously published meteorite data (Moynier et al., 2011; Schiller et al., 2014). For example, Orgueil has been analysed several times in the course of this study and is characterised by a Cr isotopic composition of $-0.145 \pm 0.012\text{‰}$ (2 s.d., $n = 6$), which is different from the previously published value ($-0.41 \pm 0.18\text{‰}$, 2 s.d., $n = 10$; Moynier et al., 2011). There are several possible reasons for this discrepancy and critically there is the difference in method used to determine the Cr isotopic composition. We use a double spike TIMS method whereas Moynier et al. (2011) and Schiller et al. (2014) used a standard sample bracketing MC-ICPMS technique. The double spike method has two clear advantages over standard sample bracketing. Firstly, it corrects for isotopic fractionation that occurs during sample preparation and analytical measurements. The chemical separation technique we and other groups use (e.g. Trinquier et al., 2008b; Bonnand et al., 2011) demonstrably does not have a 100% column yield. This is corrected for successfully using a double-spike (e.g. Bonnand et al., 2013), but sample-standard bracketing requires 100% yield, although Moynier et al. (2011) and Schiller et al. (2014) suggest they meet this requirement. Secondly, the double-spike technique corrects for instrumental mass fractionation for each individual sample, without recourse to bracketing standards and so deals with any small amounts of residual matrix elements in the

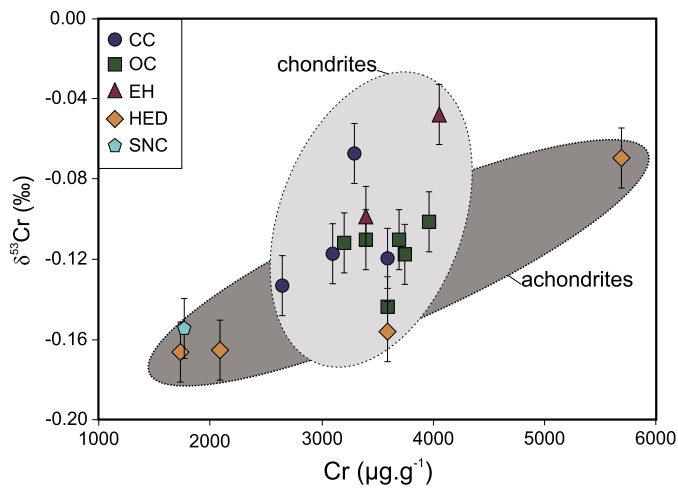


Fig. 5. Mass dependent chromium isotopic compositions versus chromium concentrations in bulk meteorites analysed in this study. SNC: shergottites–nakhilites–chassignites.

final analytical solution that would induce mass dependent fractionation in standard bracketing measurements. The issue of residual matrix elements is much harder to assess for standard-sample bracketing methods unless standards doped with the same matrix as the samples are run through the chemistry and then analysed (see Bonnand et al., 2011, 2013). This is the most likely discrepancy between the data sets and we note that organic material can be particularly problematical for standard-sample bracketing studies. It is interesting to note that the organic-rich CI1 chondrite Orgueil, has the most displaced $\delta^{53}\text{Cr}$ value (Moynier et al., 2011) from our new data. Additionally a possible origin of the discrepancy is incomplete sample dissolution. In this case, spinel is the likely mineral left after dissolution and is one of the principal Cr-bearing minerals in these samples. The technique used in this study is robust and the data can be directly compared to the BSE values obtained also by double spike techniques (Schoenberg et al., 2008). The terrestrial sample (JP-1, $\delta^{53}\text{Cr} = -0.102 \pm 0.012\text{‰}$) measured in this study is similar to previously analysed mantle xenoliths and within error of the BSE value. The data reported for the meteorite samples are also in agreement with a recent contribution by Qin et al. (2015).

Given the external reproducibility of our technique it is possible to test the hypothesis of Cr isotopic fractionation during core formation. Carbonaceous chondrites are characterised by $\delta^{53}\text{Cr}$ values ranging from -0.145 to -0.068‰ which is within error of the currently used estimate for the BSE ($-0.12 \pm 0.10\text{‰}$, Schoenberg et al., 2008, Fig. 3). Our results yield no resolvable difference between the Cr isotopic composition of chondrites and the BSE implying that Cr isotopes were not fractionated during core formation processes on Earth. Our experiments on metal–silicate partitioning of Cr are in agreement with this conclusion.

5.4. Mass dependent Cr stable isotope variations in chondrites

The results presented in this study suggest that Cr isotopes cannot be used to constrain core formation processes on Earth. However, small variations within the chondritic data set can help us understand the fundamental differences between the groups of meteorites. First of all, the ordinary chondrites are characterised by small variations compared to both carbonaceous chondrites and enstatite chondrites. Within the carbonaceous chondrites, CO is the heaviest which could relate to the redox state of CO chondrites as they are believed to be more reduced than other carbonaceous chondrites (Rubin, 1997). Similarly, one of the enstatite chondrites

(the most reduced chondrite group) has the heaviest $\delta^{53}\text{Cr}$ of all the samples we have measured. However, there is no difference in the $\delta^{53}\text{Cr}$ among LL, L and H group ordinary chondrites, which follow progressive more reduced conditions, suggesting that any redox effects on Cr isotope fractionation are subtle. However, it is noteworthy that the variability we see in only two enstatite chondrites is reflected in other stable isotope systems, notably Si, which have different compositions from other chondrite groups (Armytage et al., 2012; Savage and Moynier, 2013).

Perhaps the most striking feature of the chondritic data is the overall lack of variability compared with the BSE. Unlike the study of Moynier et al. (2011), we do not see convincing correlations with other compositional data such as $\Delta^{17}\text{O}$ and Mg/Cr ratios (not plotted), which indicates there is rather limited variability in the $\delta^{53}\text{Cr}$ composition of material that was mixed in the early solar nebular. It also suggests that magmatic processes in the Earth may have produced the greater, albeit small, range of $\delta^{53}\text{Cr}$ found in high temperature terrestrial rocks. More data are required to assess whether small variations in stable Cr isotopes in meteorites can tease out more information about the formation of primitive material in the Solar System.

5.5. Mass dependent variations in achondrites

HEDs and Martian meteorites have also been analysed in this study. They are characterised by a greater range in stable Cr isotope composition relative to those displayed by other meteorite groups. These samples are believed to be basalts from Vesta (Pasamonte, Juvinas), associated cumulates from Vesta (Johnstown) and cumulate from Mars (Nakhla). The aim was to determine the Cr stable isotope composition of Vesta and Mars mantles. However, it was recently demonstrated that Cr isotopes are fractionated by magmatic processes (Bonnand et al., in press) and therefore a direct comparison of the data and chondrite values is not possible. The correlation between Cr concentration and Cr stable isotope composition for the achondrites suggests that the samples depleted in Cr are isotopically lighter than the Cr enriched samples (Fig. 5). This is in agreement with mare basalts fractionation (Bonnand et al., in press). A suite of chemically related samples should be analysed before the Cr isotopic compositions of both Vesta and Mars' mantles can be assessed.

6. Conclusions

Seventeen meteorites samples were analysed for their radiogenic and nucleosynthetic as well as mass dependent Cr isotopic compositions. Chondrites are characterised by excesses in radiogenic ^{53}Cr as previously demonstrated. The larger variations in $\varepsilon^{54}\text{Cr}$ are within the HEDs achondrites. Large variations in $\varepsilon^{54}\text{Cr}$ are also reported with carbonaceous chondrites showing ^{54}Cr excesses compared to terrestrial samples while ordinary chondrites are ^{54}Cr depleted. Finally, enstatite chondrites have $\varepsilon^{53}\text{Cr}$ and $\varepsilon^{54}\text{Cr}$ values similar to that of the Earth. These results are similar to previously published dataset for meteoritic samples.

Five metal–silicate experiments have been performed to study the equilibrium Cr isotope fractionation between metal and silicate. There is no isotopic difference between metal and silicate, which provides evidence that Cr isotopes are unlikely to be fractionated during metal segregation. This is in agreement with Cr stable isotope compositions of chondrites which range from -0.146 to -0.048‰ , essentially identical to the current estimate of the Bulk Silicate Earth ($-0.12 \pm 0.10\text{‰}$, Schoenberg et al., 2008).

Small mass dependent Cr isotope variations are reported in bulk rock meteorites both in chondrites and achondrites. The variations in chondrites could be related to volatility and/or redox conditions but more data are required to test those hypotheses, although

the total variation in chondritic meteorites suggests the $\delta^{53}\text{Cr}$ of early solar nebular material was small ($<0.1\%$). Mass dependent Cr isotope composition is potentially a very powerful tool to constrain the chemical composition of the building blocks of the Earth. Achondrites seem to be affected by magmatic differentiation and therefore the Cr isotopic composition of Mars and Vesta cannot be fully assessed until a more extensive suite of data is acquired for these bodies, although their composition does overlap that of the bulk silicate Earth.

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