Mass dependent fractionation of stable chromium isotopes in mare basalts: Implications for the formation and the differentiation of the Moon

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Abstract

We present the first stable chromium isotopic data from mare basalts in order to investigate the similarity between the Moon and the Earth’s mantle. A double spike technique coupled with MC-ICP-MS measurements was used to analyse 19 mare basalts, comprising high-Ti, low-Ti and KREEP-rich varieties. Chromium isotope ratios ($\Delta^{53}$Cr) for mare basalts are positively correlated with indices of magmatic differentiation such as Mg# and Cr concentration which suggests that Cr isotopes were fractionated during magmatic differentiation. Modelling of the results provides evidence that spinel and pyroxene are the main phases controlling the Cr isotopic composition during fractional crystallisation. The most evolved samples have the lightest isotopic compositions, complemented by cumulates that are isotopically heavy. Two hypotheses are proposed to explain this fractionation: (i) equilibrium fractionation where heavy isotopes are preferentially incorporated into the spinel lattice and (ii) a difference in isotopic composition between Cr$^{2+}$ and Cr$^{3+}$ in the melt. However, both processes require magmatic temperatures below 1200 °C for appreciable Cr$^{3+}$ to be present at the low oxygen fugacities found in the Moon (IW − 1 to −2 log units). There is no isotopic difference between the most primitive high-Ti, low-Ti and KREEP basalts, which suggest that the sources of these basalts were homogeneous in terms of stable Cr isotopes. The least differentiated sample in our sample set is the low-Ti basalt 12016, characterised by a Cr isotopic composition of $-0.222 \pm 0.025\%e$, which is within error of the current BSE value ($-0.124 \pm 0.101\%e$). The similarity between the mantles of the Moon and Earth is consistent with a terrestrial origin for a major fraction of the lunar Cr. This similarity also suggests that Cr isotopes were not fractionated by core formation on the Moon.

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1. INTRODUCTION

It is widely accepted that the Moon formed after the collision between the proto-Earth and a Mars-sized impactor (e.g. Hartmann and Davis, 1975; Cameron and Ward, 1976) although there is still debate over whether the Moon is formed predominantly from impactor material or from the Earth’s mantle (e.g. Gessmann and Rubie, 2000;
A consistent body of evidence has accumulated demonstrating that the Earth and Moon are isotopically very similar (e.g. for the elements O, Si and Ti), despite there being considerable variability in other Solar System material, although recent studies suggest small isotopic differences between the Moon and the Earth (Herwartz et al., 2014; Kruijer et al., 2015). The canonical Giant Impact between the proto-Earth and the impactor, Theia, generates most of the Moon’s atoms from the impacting planet Theia (Canup, 2004). Several models have been proposed to explain the isotopic similarities between the Earth and Moon: both bodies were formed at similar heliocentric distances (Wiechert et al., 2001); the lunar mantle is made of Earth material (Zhang et al., 2012); the proto lunar disc equilibrated with the Earth (Pahlevan and Stevenson, 2007; Armettage et al., 2012); the solar system is homogeneous inward of Earth’s orbit (Dauphas et al., 2014; Mastrobuono-Battisti et al., 2015) or the canonical simulations are incorrect (Cuk and Stewart, 2012; Canup, 2012; Reufer et al., 2012).

The chemical compositions of lunar rocks (meteorites and Apollo and Luna samples) provide some primary constraints on processes responsible for the formation and the differentiation of the Moon (e.g. Warren and Taylor, 2014) and early Earth (e.g. Caro, 2011). Differentiation of the Moon resulted in an anorthositic crust, mantle (solid upper mantle, with some evidence of partially molten lowermost mantle) and core (solid inner core and fluid outermost core) (Wieczorek et al., 2013) and it has been proposed that the Moon experienced a two-stage differentiation event (Warren, 1985). Firstly, in the aftermath of the Giant Impact, the lunar surface was completely molten and was covered in a putative lunar magma ocean (LMO) that extended to the depths of several hundred kilometres. The LMO differentiated to produce a dense ultramafic mantle (olivine and pyroxene) and a light plagioclase-rich crust and under more reduced conditions (Chabot and Agee, 2003; Papike et al., 2005) and spectroscopic studies indicate the presence of significant amounts of Cr$^{2+}$ at high temperatures (Papike et al., 2005) and spectroscopic studies indicate the presence of significant amounts of Cr$^{2+}$ at high temperatures (Papike et al., 2005). The key finding from these studies is that the isotopic composition of the Moon and the Earth are similar for refractory elements while some volatile elements (e.g. Zn, Cl) have a different isotopic composition. In detail, there are compositional differences between low-Ti and high-Ti basalts for some stable isotope systems (e.g. O, Fe, Si, Mg, Cd, Zn, Cl) of lunar samples (e.g. Wiechert et al., 2001; Moynier et al., 2006; Magna et al., 2006; Schediwy et al., 2006; Spicuzza et al., 2007; Hallis et al., 2010; Liu et al., 2010; Sharp et al., 2010; Armettage et al., 2012; Paniello et al., 2012; Day and Moynier, 2014; Herwartz et al., 2014). The key finding from these studies is that the isotopic composition of the Moon and the Earth are similar for refractory elements while some volatile elements (e.g. Zn, Cl) have a different isotopic composition. In detail, there are compositional differences between low-Ti and high-Ti basalts for some stable isotope systems (e.g. O, Fe, Si, Mg, Cd, Zn, Cl) of lunar samples (e.g. Wiechert et al., 2001; Moynier et al., 2006; Magna et al., 2006; Schediwy et al., 2006; Spicuzza et al., 2007; Hallis et al., 2010; Liu et al., 2010; Sharp et al., 2010; Armettage et al., 2012; Paniello et al., 2012; Day and Moynier, 2014; Herwartz et al., 2014). The key finding from these studies is that the isotopic composition of the Moon and the Earth are similar for refractory elements while some volatile elements (e.g. Zn, Cl) have a different isotopic composition. In detail, there are compositional differences between low-Ti and high-Ti basalts for some stable isotope systems (e.g. O, Fe, Si, Mg, Cd, Zn, Cl) of lunar samples (e.g. Wiechert et al., 2001; Moynier et al., 2006; Magna et al., 2006; Schediwy et al., 2006; Spicuzza et al., 2007; Hallis et al., 2010; Liu et al., 2010; Sharp et al., 2010; Armettage et al., 2012; Paniello et al., 2012; Day and Moynier, 2014; Herwartz et al., 2014). The key finding from these studies is that the isotopic composition of the Moon and the Earth are similar for refractory elements while some volatile elements (e.g. Zn, Cl) have a different isotopic composition.
In the reduced lunar interior chromium is dominantly present as Cr$^{2+}$ (Papike et al., 2005). Consequently, the differences in oxygen fugacity between the Earth and the Moon can lead to different behaviour of Cr during magmatic processes such as partial melting and/or fractional crystallisation. For example, it has been argued that the higher Cr concentrations in mare basalts (~4000 µg g$^{-1}$) compared to terrestrial basalts (~500 µg g$^{-1}$; Basaltic Volcanism Study Project, 1981) could be due to the fact that Cr is less compatible under low $fO_2$ conditions (Roeder and Reynolds, 1991).

Chromium isotopes provide a further means to explore the geochemical behaviour of Cr in the Moon and Earth. Isotopic variation may be related to either mass independent or mass dependent processes. Mass independent variations are due to either radiogenic decay of $^{53}\text{Mn}$ to $^{53}\text{Cr}$ (half-life 3.7 Ma) and/or production of the neutron-rich isotope $^{54}\text{Cr}$ in type Ia supernova, which produce shifts in $^{53}\text{Cr}/^{52}\text{Cr}$ and $^{54}\text{Cr}/^{52}\text{Cr}$ ratios, respectively (Birck and Allègre, 1988; Lugmair and Shukolyukov, 1998; Trinquier et al., 2007, 2008; Moynier et al., 2007; Yin et al., 2007; Qin et al., 2010). Surprisingly only a limited number of analyses have been made on lunar samples (Lugmair and Shukolyukov, 1998; Qin et al., 2010) but these studies reached the same conclusion that there is no difference between the terrestrial and lunar mantle for mass independent Cr isotopes at the level of analytical uncertainty. This suggests that the Moon and Earth homogenised after the extinction of $^{53}\text{Mn}$, or that both the impactor and the proto-Earth had similar Mn/Cr ratios and $^{53}\text{Mn}$ abundance. Similarly the lack of difference in $^{54}\text{Cr}/^{52}\text{Cr}$ ratios suggests a provenance for the impactor and the proto-Earth and/or complete homogenisation.

To date, there is no mass-dependent Cr isotope study of lunar rocks, but the knowledge that lunar and terrestrial rocks do not differ in mass-independent Cr isotopes means that the two bodies must lie on a common mass fractionation trend in Cr isotope space. Mass dependent (stable) chromium isotope variation is expressed in $\delta$ notation relative to NBS979 chromium standard ($\delta^{53}\text{Cr} = ([^{53}\text{Cr}]^{\text{sample}}/[^{53}\text{Cr}]^{\text{NBS979}} - 1) \times 1000$) (Ellis et al., 2002). Schoenberg et al. (2008) determined the Cr isotopic composition of the bulk-silicate Earth using a double-spike technique and demonstrated it has a rather restricted composition ($\delta^{53}\text{Cr} = -0.124 \pm 0.101\text{‰}$, Schoenberg et al., 2008) indicating no Cr isotopic fractionation during partial melting at the level of their analytical uncertainties. Recent studies of mass dependent Cr isotopes in meteorites measured by sample-standard-bracketing techniques (Fig. 1, Moynier et al., 2011; Schiller et al., 2014) report small fractionations between meteorites and the bulk-silicate Earth (BSE) (Fig. 1). Moynier et al. (2011) proposed that Cr isotopic fractionation occurs during core formation with light isotopes preferentially incorporated into metallic liquids whereas Schiller et al. (2014) ascribe the difference between the Earth and chondritic meteorites as simply a reflection of heterogeneity in the early Solar System material rather than terrestrial core formation. By contrast three recent double-spike Cr isotope studies reveal no resolvable difference between terrestrial and meteoritic samples

![Fig. 1. Compilation of Cr isotopes data from the literature together with the data presented in this study. Data for granite, basalts and ultramafic rocks and cumulates are from Schoenberg et al. (2008). The meteorites data are from Moynier et al. (2011) (full circles) and Schiller et al. (2014) (open circles). The lunar data are from this study. The grey vertical bar defines the estimated range for the BSE value (~0.124 ± 0.101‰, Schoenberg et al., 2008).](image-url)
Average low-Ti

| Apollo mission | Sample number | Sample Type | \( \delta^{53}\text{Cr} \) | 2 s.d. | Cr | TiO\textsubscript{2} | MgO | FeO | Mg# |
|----------------|---------------|-------------|----------------|--------|---|-------------|-----|-----|-----|
| JP-1           | High-Ti       | -0.128      | 0.022          |        |   | 11.72       | 7.15 | 20.18| 40.9 |
| 12             | Low-Ti        | -0.216      | 0.022          | 2330   | 11.68 | 7.74       | 19.08| 42.8 |
| 12050          | High-Ti       | -0.263      | 0.022          | 2250   | 11.51 | 7.47       | 20.24| 40.2 |
| 12057          | High-Ti       | -0.211      | 0.022          | 2190   | 11.27 | 7.47       | 20.24| 40.2 |
| 12058          | High-Ti       | -0.274      | 0.022          | 1410   | 8.16 | 6.11       | 18.46| 41.1 |
| 12072          | High-Ti       | -0.271      | 0.022          | 2390   | 11.89 | 7.61       | 20.03| 37.6 |
| 12016          | Low-Ti        | -0.178      | 0.022          | 3700   | 13.73 | 9.64       | 19.18| 48.7 |
| 12040          | Low-Ti        | -0.227      | 0.022          | 3830   | 12.74 | 10.1       | 18.53| 50.1 |
| 12053          | High-Ti       | -0.171      | 0.022          | 2570   | 12.91 | 8.13       | 16.45| 45.8 |
| 12021          | Low-Ti        | -0.229      | 0.074          |        |   | 13.52       | 23.36| 51.8 |
| 12051          | Low-Ti        | -0.147      | 0.022          | 3650   | 2.66 | 16.40       | 23.05| 56.9 |
| 12052          | Low-Ti        | -0.329      | 0.022          | 1720   | 4.45 | 6.51        | 21.11| 37.0 |
| 12053          | Low-Ti        | -0.191      | 0.022          | 2990   | 3.29 | 7.68        | 20.36| 41.0 |
| 12057          | Low-Ti        | -0.242      | 0.022          | 1950   | 3.66 | 6.37        | 19.51| 37.9 |
| 14             | Low-Ti        | -0.238      | 0.022          | 2100   | 2.60 | 7.81        | 16.88| 46.6 |
| 15             | Low-Ti        | -0.151      | 0.022          | 6080   | 2.09 | 11.76       | 23.29| 48.5 |
| 15386          | KREEP basalt  | -0.158      | 0.022          | 2040   | 2.05 | 8.19        | 10.6 | 59.3 |
| 15555          | Low-Ti        | -0.203      | 0.022          | 4280   | 1.10 | 12.28       | 19.52| 54.4 |

Average high-Ti

| Apollo mission | Sample number | Sample Type | \( \delta^{53}\text{Cr} \) | 2 s.d. | Cr | TiO\textsubscript{2} | MgO | FeO | Mg# |
|----------------|---------------|-------------|----------------|--------|---|-------------|-----|-----|-----|
| 12             | Low-Ti        | -0.222      | 0.022          | 3680   | 3.72 | 13.52       | 23.36| 51.8 |
| 12040          | Low-Ti        | -0.147      | 0.022          | 3650   | 2.66 | 16.40       | 23.05| 56.9 |
| 12051          | Low-Ti        | -0.329      | 0.022          | 1720   | 4.45 | 6.51        | 21.11| 37.0 |
| 12052          | Low-Ti        | -0.191      | 0.022          | 2990   | 3.29 | 7.68        | 20.36| 41.0 |
| 12053          | Low-Ti        | -0.242      | 0.022          | 1950   | 3.66 | 6.37        | 19.51| 37.9 |
| 15             | Low-Ti        | -0.238      | 0.022          | 2100   | 2.60 | 7.81        | 16.88| 46.6 |
| Average low-Ti |               | -0.215      | 0.058          |        |   |             |     |     |     |

broad (12016, 12051 and 12064) and pigeonite basalt (12052). Apollo 14 sample (14053) is a group C basalt and finally, the Apollo 15 basalts are olivine normative (15016 and 15555) and a KREEP basalt (15386) (Chappell and Green, 1973). The high-Ti samples analysed in this study were collected during the Apollo 11 and 17 missions (Table 1).

Lunar basalts analysed in this study span a range of Mg# (molar Mg/(Mg + Fe) ratio) from 33 to 57 and TiO\textsubscript{2} concentration from 1.14 to 13.03 wt.%, which would allow the study of Cr isotopes during magmatic differentiation. Sample 12040 has been described as an olivine-cumulate (Baldridge et al., 1979) and therefore does not represent a primary melt composition.

3. ANALYTICAL METHODS

Protocols for the separation of Cr from geological and environmental samples have been previously published (e.g. Ball and Izbicki, 2004; Trinquier et al., 2008; Bonnand et al., 2011, 2013). As we already know that there is no noticeable difference in mass independent Cr isotopes between the Moon and Earth (see introduction) the stable Cr isotopic composition can be determined solely from a double-spike analyses (Schoenberg et al., 2008; Bonnand et al., 2011). A summary of the method used in this study is given below.

3.1. Sample dissolution and chemical separation

Approximately 10 mg of whole rock powder was digested using concentrated HNO\textsubscript{3}-HF-HCl acid mixtures. The fully dissolved sample was evaporated to dryness and then re-dissolved in 6 M HCl. An aliquot of ~1 μg of chromium was spiked with a requisite amount of \( ^{50}\text{Cr}-^{54}\text{Cr} \) double spike (Bonnand et al., 2011) and the solutions were then dried down and taken up again in 6 M HCl to ensure equilibrium between the spike and the sample before chemical separation. The protocol used to separate the Cr fraction from the matrix is a two column procedure. The first column is designed to separate Cr from the main cations in the matrix (e.g. Ca, Na, Mg) and a full description of this chemical separation technique is presented in Bonnand et al. (2011). Briefly, 2.9 ml of AG50 X8 (200–400 mesh chloride form resin) was added to a 30 ml PFA column and the sample is loaded and eluted in 0.5 M HCl. The Cr fraction and a small amount of other minor elements such as Ti, pass straight through the column and are collected during this first elution. In order to clean the Cr fraction from any elements with isobaric interferences (Ti, V and Fe), a second column chemistry was performed. The Cr fraction was dried down and dissolved in 0.5 M HNO\textsubscript{3}. A disposable Bio-Rad Poly-Prep column was filled with 1 mL of cationic AG50 X8 (200–400 mesh chloride form resin) was added to a 30 ml PFA column and the solution was then loaded and eluted in 0.5 M HCl. The Cr fraction and a small amount of other minor elements such as Ti, pass straight through the column and are collected during this first elution. In order to clean the Cr fraction from any elements with isobaric interferences (Ti, V and Fe), a second column chemistry was performed. The Cr fraction was dried down and dissolved in 0.5 M HNO\textsubscript{3}. A disposable Bio-Rad Poly-Prep column was filled with 1 mL of cationic AG50 X8 (200–400 mesh chloride form resin) was added to a 30 ml PFA column and the sample is loaded and eluted in 0.5 M HCl. The Cr fraction and a small amount of other minor elements such as Ti, pass straight through the column and are collected during this first elution. In order to clean the Cr fraction from any elements with isobaric interferences (Ti, V and Fe), a second column chemistry was performed. The Cr fraction was dried down and dissolved in 0.5 M HNO\textsubscript{3}. A disposable Bio-Rad Poly-Prep column was filled with 1 mL of cationic AG50 X8 (200–400 mesh chloride form resin) was added to a 30 ml PFA column and the sample is loaded and eluted in 0.5 M HCl. The Cr fraction and a small amount of other minor elements such as Ti, pass straight through the column and are collected during this first elution.
chemical purification procedure is ∼0.2 ng, which is negligible compared to the 1000 ng processed through the columns.

### 3.2. Mass spectrometry

Chromium isotopic analyses were performed with a ThermoFisher Neptune multi-collector inductively coupled plasma mass spectrometer (MC-ICP-MS) at the Open University (UK). Solutions were introduced into the mass spectrometer using an Aridus II desolvator system. Detailed description of the setting used for the Cr isotopes measurements has been previously given (Bonnand et al., 2011). A solution of 100 ppb was used and a sensitivity of ∼200 V ppm⁻¹ was routinely obtained. A total of 200 cycles were measured for each analysis. Chromium isotope measurements were performed in medium mass resolution mode (ΔM/M > 5500), which ensures that polybaric interferences are resolved from the isotopes of interest. Potential polybaric interferences from Fe, Ti and V were monitored on masses 56Fe, 50Ti and 51V, and 54Cr and 53Cr signals were corrected for isobaric contributions, although these corrections were always negligible and within the internal uncertainty of the δ53Cr measurements. An instrumental ‘on-mass’ background was determined by measuring the same 0.3 M HNO3 used to dissolve the samples before each sample and standard measurement. The instrumental background was then subtracted from each corresponding standard and sample runs and was less than 0.1% of the total signal.

### 4. RESULTS

#### 4.1. Reproducibility and accuracy

Previous studies have demonstrated that high-temperature processes can fractionate heavy stable isotopes (M > 30, e.g. Schauble, 2004; Weyer et al., 2005) and therefore chromium isotopes have the potential to be fractionated by different processes such as redox reactions, partial melting and fractional crystallisation. However, fractionation at high temperatures is expected to be smaller than that at low temperatures and therefore we have developed a new high-precision method to measure Cr isotopic composition in high-temperature rocks to resolve any variations.

The accuracy of our method was determined with multiple measurements of the NBS SRM 979 Cr standard, spiked and then processed through chemistry and analysed in the same way as a sample. The δ53Cr values obtained from these experiments are δ53Cr = −0.003 ± 0.011‰ (2 standard deviation, n = 4). The reproducibility of the mass spectrometer analyses was assessed with multiple measurements of a spiked NBS SRM 979 solution (δ53Cr = 0.000 ± 0.014‰, 2 s.d., n = 116). The external reproducibility was determined by multiple measurements of a peridotite standard (JP-1) over a four months period and is −0.128 ± 0.022‰ (2 s.d., n = 14). The internal precision for individual runs is always lower than the external reproducibility and the latter is used for the samples investigated in this study. The uncertainty associated with the fractionation law used in the double spike deconvolution procedure (difference between kinetic and equilibrium fractionation laws) was propagated (Schoenberg et al., 2008; Bonnand et al., 2011), but as all the samples analysed in this study have δ53Cr values within 0.4‰ of NBS SRM 979, the choice of fractionation law produces minimal additional uncertainty (∼0.004‰). The methods described in this paper provide a factor of 2.5 improvement in precision compared to our previous work (Bonnand et al., 2011) and we can therefore study the smaller differences in δ53Cr which are expected in silicate samples (Schoenberg et al., 2008; Farkas et al., 2013).

#### 4.2. Chromium concentrations and chromium isotopes in mare basalts

The Cr concentrations in the mare basalts analysed in this study range from 1410 to 6075 µg g⁻¹ (Table 1, Fig. 2; Hallis et al., 2014). There is a positive correlation between Cr concentration and Mg# for both Apollo 12 (Fig. 2a) and Apollo 11 (Fig. 2b) samples. There is also a good correlation between Cr concentration and TiO2 concentration.

The Cr isotopic compositions of lunar samples analysed in this study are reported in Table 1 together with other
geochemical data. Lunar samples are characterised by relatively small variation in $\delta^{53}$Cr from $-0.329$ to $-0.147\%e$ (Fig. 1), but overall, lunar samples are characterised by lighter $\delta^{53}$Cr compared to the bulk-silicate Earth ($-0.124 \pm 0.101\%e$, Schoenberg et al., 2008), and double spike data for meteorites (Bonnand et al., 2016), although there is some clear overlap in composition. Nevertheless, the lunar samples have slightly more positive $\delta^{53}$Cr than the chondritic meteorite data of Moynier et al. (2011) and Schiller et al. (2014) (Fig. 1). Chromium isotopes in all the lunar samples have slightly more positive $\delta^{53}$Cr than the chondritic meteorite data of Moynier et al. (2011) and Schiller et al. (2014) (Fig. 1). Chromium isotopes in all the lunar samples have slightly more positive $\delta^{53}$Cr than the chondritic meteorite data of Moynier et al. (2011) and Schiller et al. (2014) (Fig. 1). Chromium isotopes in all the lunar samples have slightly more positive $\delta^{53}$Cr than the chondritic meteorite data of Moynier et al. (2011) and Schiller et al. (2014) (Fig. 1).

**Fig. 3.** Cr isotopic composition versus Mg# (a), Cr concentration (b) and TiO$_2$ (c) in mare basalts analysed in this study. The BSE value is from Schoenberg et al. (2008), (solid line is the mean and dotted line is ±2.s.d; see text for details).

In this section we first discuss the behaviour of chromium in lunar basalts, followed by the Cr isotope fractionation during magmatic differentiation on the Moon. We then estimate the average Cr isotopic composition of the lunar mantle and finally we discuss the implications for the formation of the Moon and its differentiation.

### 5. DISCUSSION

The Cr concentrations in mare basalts range from 1410 $\mu$g g$^{-1}$ to 6075 $\mu$g g$^{-1}$ which is higher than the average Cr concentration in primitive terrestrial basalts ($\sim 500$ $\mu$g g$^{-1}$, Basaltic Volcanism Study Project, 1981). Redox conditions control the amount of Cr in a basaltic melt and reduced melts are enriched in Cr (Roeder and Reynolds, 1991; Hanson and Jones, 1998; Kamenetsky et al., 2001). At the low fO$_2$ (IW-2) present in the Moon, Cr$^{2+}$ will be the dominant species of Cr, with Cr$^{2+}$/Cr$_{TOT}$ ratios of $\sim 0.9$ (Berry et al., 2006) expected in primary melts. Elevated Cr concentrations in lunar melts have several consequences for the mineral chemistry and melt evolution of lunar rocks. Lunar olivine is enriched in Cr compared to terrestrial olivine (Papike et al., 1976) as both Cr$^{2+}$ and Cr$^{3+}$ can be incorporated into the olivine lattice and its concentration in olivine depends dominantly on Cr concentration in the melt (Papike et al., 2005). Partitioning studies indicate that Cr$^{2+}$ is incorporated more readily into pyroxenes than olivine (Li et al., 1995). While it is difficult to accurately gauge the proportion of Cr$^{2+}$ to Cr$^{3+}$ in lunar...
pyroxene from electron microprobe analyses, charge balance calculations suggest that many pyroxene analyses are consistent with Cr$^{2+}$ being present (Hallis, 2010) and therefore the large modal abundance of pyroxene in the samples we have analysed means pyroxene is a significant sink for Cr during fractionation. Although Cr$^{2+}$ is the main Cr species in lunar melts, it has long been recognised that some Cr must be present as Cr$^{3+}$ (e.g. Seifert and Ringwood, 1988) because a variety of Cr-rich oxide phases including chromium-spinel, high-Ti chromium spinel and Cr-rich ulvöspinel are minor phases in the Apollo samples (Haggerty and Meyer, 1970; El Goresy et al., 1971; Papike et al., 1976; Hallis, 2010; Hallis et al., 2010). All these phases strongly favour Cr$^{3+}$ over Cr$^{2+}$ so either the lunar melts have to decrease their Cr$^{2+}$/Cr$^{3+}$ ratio sufficiently to allow spinel crystallisation, or the Cr concentration of the spinel saturation surface becomes low enough to intersect the Cr$^{3+}$ content of the melt. Both these requirements are met when the temperature of the melt is reduced below 1200 °C as low-temperatures favour lower Cr$^{2+}$/Cr$^{3+}$ ratios (Schreiber and Haskin, 1976; Berry et al., 2006) also lowering the spinel-saturation concentration to below 700 μg g$^{-1}$ (Roeder and Reynolds, 1991; Hanson and Jones, 1998). This is consistent with experimental studies (Longhi, 1987, 1992), thermodynamic data (Li et al., 1995) and petrographic and mineralogical observations (e.g. Papike et al., 1976; Longhi, 1987) that Cr-rich oxide phases are commonly found associated with late-stage crystallising phases in lunar basalt. It should be noted that there is petrographic and mineral chemistry evidence for early crystallisation of chromite in some lunar basalts (e.g. Haggerty and Meyer, 1970). Chromite inclusions have been found in olivine and pyroxene and chromites in the groundmass are often mantled with Cr-rich ulvöspinel. However, the proportion of chromite crystallisation must be extremely small, because Cr concentrations tend to increase rather than decrease during magmatic differentiation of primitive lunar basalts (see below).

Modal analysis indicates that pyroxene is the most abundant Cr-bearing mineral in lunar basalts, although not necessarily the most important carrier of Cr. For example the low-Ti basalt 12016 has 52% clinopyroxene and 1.6% spinel that correspond to 40% and 54% of total Cr inventory, respectively (Table 2). Feldspar, olivine and ilmenite are relatively abundant in 12016 with modal abundances of 29.1%, 12% and 4.8% respectively (Table 2, Hallis et al., 2010). However, their contribution to the Cr budget is small (0% for feldspar, 1.4% for olivine and 2.1% for ilmenite). Therefore, it is clear that the Cr budget in low-Ti basalt is controlled by pyroxenes and spinel. Taking the Apollo 12 basalts as an example of the low-Ti basalts, which are characterised by a positive correlation between their Cr concentration and Mg# (Fig. 2a), these data have been interpreted as resulting from fractional crystallisation of olivine, clinopyroxene and spinel from a “primary volcanic glass” composition (Delano, 1979). It has been suggested that Cr concentrations increase from 4000 μg g$^{-1}$ to about 5500 μg g$^{-1}$ due to crystallisation of olivine (Delano, 1979). Using a partition coefficient of Cr between olivine and melt of about 0.85 (Hanson and Jones, 1998), a Fe-Mg olivine-melt coefficient of 0.3 (Roeder and Emslie, 1970) and a simple Rayleigh fractionation model involving olivine could explain the increase in Cr observed in the Apollo 12 basalts, but would produce a much larger decrease in Mg# than is observed. We therefore argue that the Cr concentration variations in primary lunar basalts probably reflect both early olivine fractionation and Cr concentration heterogeneities in the source regions of low-Ti basalts. During fractional crystallisation of spinel and pyroxene, the Cr concentration in the residual melt will decrease because of the compatible behaviour of Cr in these phases ($D$ in spinel = 50 and $D$ in pyroxene = 2.5; Seifert and Ringwood, 1988). The decrease in Cr concentration in low-Ti basalts, with decreasing Mg# (Fig. 2), can be explained by the fractional crystallisation of first pyroxene, followed by pyroxene and spinel together (Fig. 4). By contrast, the crude negative correlation between MgO concentration and TiO$_2$ in the low-Ti basalts (Fig. 4a) indicates that Ti is behaving as an incompatible element and so the spinel phase must be a low-Ti chromium spinel (TiO$_2$ < 10 wt. %), which is commonly found in the low-Ti lavas (Papike et al., 1976; Hallis, 2010). Compilations of liquid line of descents for low-Ti lunar suites confirm that Ti behaves as a mildly incompatible element over a wide range of MgO contents (see Longhi, 1987; Hauri et al., 2015).

A model for the later crystallisation of the low-Ti lavas is that the most evolved samples crystallise below 1200 °C (see Longhi, 1987) and the Cr$^{2+}$/Cr$_{TOT}$ ratio is 0.6–0.7, so that for lavas with 2500–3000 μg g$^{-1}$ Cr, the amount of Cr$^{3+}$ is high enough (~700 μg g$^{-1}$, Roeder and Reynolds, 1991) for spinel to be saturated. A significant number of Cr-spinels in lunar melts have Cr# (molar Cr/(Cr + Al) ratio) of 0.69 ± 0.03 with Mg# of less than 0.30 (see El Goresy et al., 1971; Papike et al., 1976; Hallis, 2010) consistent with crystallisation from a low-Mg# melt at temperatures of ~1150 °C (utilising the Fe-Mg partitioning data of Ballhaus et al., 1991). While, low-Mg# in some spinels may reflect low-temperature re-equilibration with silicate phases, the prevalence of these spinel compositions suggests that much of the Cr-rich spinel crystallised late. A small amount of crystallisation of spinel (1%) will remove the majority of Cr$^{3+}$ from the melt while still retaining 1500–2000 μg g$^{-1}$ Cr in the residual melt (Fig. 4).

The Cr-bearing minerals in high-Ti basalts are the same as for low-Ti basalts except that high-Ti (10–20 wt.% TiO$_2$) Cr-rich spinels and Cr-ulvöspinel (>20 wt.% TiO$_2$) are also common and there is substantial ilmenite crystallisation, although it plays a limited role in fractionating Cr. In high-Ti basalts, the Cr concentrations are positively correlated with Mg# in the same way as the Apollo 12 basalts (Fig. 2b), but by contrast Cr has a crude positive correlation with TiO$_2$, suggesting Ti behaves as a compatible element (Fig. 4b) at the MgO contents found in these lavas (Longhi, 1987; Hauri et al., 2015). Ilmenite and the high-Ti Cr-spinel are most likely late phases in the crystallisation sequence of high-Ti basalts (Longhi, 1987) and weak positive correlation between Cr and TiO$_2$ most likely represents variation in the proportion of ilmenite/spinel and pyroxene depending on melt composition. In summary, the decreasing Cr content of evolved lunar melts cannot be produced
by pyroxene crystallisation alone, but also requires the stabilisation of Cr$^{3+}$ bearing oxide phases at temperatures below 1200 °C.

### 5.2. Chromium isotope fractionation during fractional crystallisation

Utilising the mare basalts to get back to the primary isotopic composition of the source rocks requires an exploration of any isotopic fractionation during processes such as partial melting and fractional crystallisation that may have modified the Cr isotopic signature in mare basalts. In the case of Cr, although partial melting on Earth is associated with a change in oxidation state of Cr from Cr$^{3+}$ to Cr$^{2+}$ (Berry et al., 2006), it has been suggested that partial melting does not fractionate Cr isotopes (Schoenberg et al., 2008) as both basalts and peridotites have similar compositions. On the Moon, the Cr$^{3+}$/Cr$^{4+}$OT is higher compared to the Earth and unlikely to change during partial melting of the lunar mantle. Therefore isotopic fractionation between source rocks and melts during partial melting on the Moon is also likely to be negligible. In other words, it is possible to use the Cr isotopic composition of mare basalts to reconstruct the isotopic composition of their source regions.

The second process that could modify the primary Cr isotopic composition of the lunar basalts is fractional crystallisation. Unlike a suite of lavas from a single volcano on Earth it is more difficult with lunar samples to verify the chemical relationship between the different samples analysed, although the data for Apollo 12 provide the most coherent set of data that we have analysed (12016, 12052 and 12064 are assumed to be chemically related with 12016 representing the primary sample and 12064 is the most evolved (Hallis et al., 2014, Table 1, Fig. 2). The broad positive correlation between Cr isotopic composition and Mg# (Fig. 3a) suggests that Cr isotopes are fractionated during fractional crystallisation on the Moon with the crystallising phases being isotopically heavy relative to the melt and the Cr isotopic composition of the melt becomes lighter during magmatic differentiation (Fig. 5). Theoretical modelling presented in Moynier et al. (2011) illustrates the equilibrium fractionation of Cr between different phases at equilibrium with Fe-Cr metal. Chromium isotopic composition of spinel is heavier compared to silicates (olivine and pyroxene) by about 0.15‰ at magmatic temperatures (1200–1400 °C) and therefore is the most likely phase to cause the Cr isotopic variation observed in the lunar samples.

As described in the previous section, the Cr-MgO trends can be reproduced by fractional crystallisation (Fig. 4b). Specifically, samples below ~2500 µg g$^{-1}$ Cr require crystallisation of a Cr-rich oxide phase because the drop in Cr for a given drop in MgO cannot solely be explained by pyroxene fractionation. If samples are grouped according to whether they have greater or less than 2500 µg g$^{-1}$ Cr irrespective of Ti content), they are statistically different indicating that a Cr-rich oxide phase is the most likely phase in producing the light $^{53}$Cr common observed in evolved lunar basalts (Fig. 5a). Applying a simple Rayleigh fractionation model, utilising the phase proportions from the fractionation model (see Fig. 4b) for a range of fractionation factors (the fractionation factor, $\Delta^{53}$Cr, is the difference in isotopic composition between the melt and the crystals), can produce the full range of isotopic values measured in lunar samples if $\Delta^{53}$Cr is small (<0.1‰, Fig. 5b).

If the $\Delta^{53}$Cr was fixed to 0.05 then pyroxene followed by pyroxene + spinel crystallisation can explain the light $^{53}$Cr observed in the evolved Apollo 12 samples (Fig. 5b). Much of the fractionation can be accommodated by <1% spinel fractionation with a $\Delta^{53}$Cr of ~0.15 (Fig. 5c), a value more consistent with the data of Moynier et al. (2011), if the spinel removes the majority of Cr$^{3+}$. Similarly, light $^{53}$Cr is found in high-Ti lavas through crystallisation of Cr-rich ulvospinel although the Cr-$^{53}$Cr systematics are less obvious because Cr-rich ulvospinels may crystallise from a wider range of bulk compositions. However, it should be noted that the limited number of co-genetic samples makes detailed modelling difficult, but a first-order observation is
that the data are consistent with crystallisation of a Cr-rich phase with a heavy $\delta^{53}$Cr composition. If these interpretations are correct, the Cr isotopic composition of Cr-spinel is heavier than the melt and this can be explained by two mechanisms. The first is that Cr-spinel is heavier because of equilibrium fractionation between the melt and spinel. Chromium bond-length (which is linked to the oxidation state) and the coordination number in the mineral structure control the amount of equilibrium fractionation. In the case of spinel, the preference for Cr$^{3+}$ and its location in the octahedral site potentially produce greater isotopic fractionation. A second hypothesis is that Cr$^{3+}$ in the melt is heavier than Cr$^{2+}$. During fractional crystallisation of spinel, Cr$^{3+}$ will be preferentially taken by the crystallising phase resulting in an isotopically heavy spinel relative to the melt. Further experimental work is required to unravel which mechanism is the most likely.

Fig. 4. TiO$_2$ concentration (a) and Cr concentration (b) versus MgO concentration for Apollo 11, 12 and 17 samples analysed in this study. The concentration data is from Hallis et al. (2014). The black arrows in (a) show the chemical evolution during fractional crystallisation indicating the high-Ti samples record an inflection point whereby ilmenite starts to crystallise whereas in the low-Ti samples TiO$_2$ behaves as a mildly incompatible element. The black line in (b) is a model of fractional crystallisation for the low-Ti Apollo 12 samples. The high-Ti Apollo 11 and 17 samples also define a trend where Cr concentrations are controlled by pyroxene and spinel fractionation. Ol: olivine; Px: pyroxene; Sp: spinel. Model is based on Longhi (1992) and Hauri et al. (2015) and uses a Fe–Mg partition coefficient of 0.3 for olivine (Roeder and Emslie, 1970), 0.32 for pyroxene (e.g. Kinzler and Grove, 1992) and spinel partitioning consistent with Ballhaus et al. (1991). Chromium partitioning is from Hanson and Jones, 1998 and Seifert and Ringwood (1988) (see text).

Fig. 5. (a) Histogram and calculated cumulative frequency of $\delta^{53}$Cr values for low-Ti and high-Ti basalts analysed in this study. The two groups of samples were selected based on their Cr concentration (<2500 or >2500 µg g$^{-1}$, see text for details). The vertical grey bar is the BSE value from Schoenberg et al. (2008). (b) Simple Rayleigh fractionation of Cr isotopes during fractional crystallisation as a function of Cr remaining in the melt (F$_{melt}$). The horizontal grey area is the range of values for mare basalts analysed in this study. The four lines are different $\Delta^{53}$Cr ($\delta^{53}$Cr$_{melt}$–$\delta^{53}$Cr$_{mineral}$) values used in the calculation. (c) Plot of Apollo 12 mare basalts and are Rayleigh fractionation models during fractional crystallisation assuming $\Delta^{53}$Cr = −0.05‰, −0.1‰ and −0.15‰. The lines are labelled with the proportion of Cr-spinel crystallised. The $\delta^{53}$Cr of the melt ($\delta^{53}$Cr$_{melt}$) is calculated using $\delta^{53}$Cr$_{melt} = (\delta^{53}$Cr$_{initial} + 1000) * F_{melt} - 1000$ where $\delta^{53}$Cr$_{initial}$ is the initial stable Cr isotope composition and $F_{melt}$ is the fraction of Cr remaining in the melt.
5.3. Similarities in $\delta^{53}\text{Cr}$ between high-Ti and low-Ti basalts

The low-Ti and high-Ti basalts have an average Cr isotopic composition of $-0.215 \pm 0.058\%$ and $-0.229 \pm 0.074\%$ respectively (Table 1). However, the samples analysed in this study have been fractionated relative to their sources. Nevertheless, the least differentiated samples for both suites of sample are within error of each other and this suggests that the sources of these basalts have the same Cr isotopic composition. This observation differs from some other isotope systems such as those of Fe and O (e.g. Liu et al., 2010), where the difference in isotopic composition between high-Ti and low-Ti mare basalt, has been linked to the presence of ilmenite in the source of high-Ti basalts (e.g. Elardo et al., 2011). The homogeneity in Cr isotopic compositions of the source regions of high- and low-Ti basalts is also supported by the lack of isotopic differences between low-Ti basalt and the KREEP basalt. It is best explained, if there has been little or no Cr-spinel fractionation in the KREEP sample consistent with the high Mg#. The KREEP basalt is the melting product of the urKREEP source, which is in turn the residue of the lunar magma ocean. Although Cr isotopes are fractionated during magmatic differentiation it is perhaps surprising that both the residues and cumulates of the LMO differentiation have the same isotopic composition as low-Ti basalts.

The lack of difference in Cr isotopes between primitive low-Ti, high-Ti and KREEP basalts suggests that there was limited Cr isotope fractionation during the LMO differentiation. This could be explained by a lack of spinel crystallisation during LMO differentiation, as the high temperatures favour high $\text{Cr}^{2+}/\text{Cr}_{\text{TOT}}$ ratios, which limit spinel crystallisation. Perhaps more likely is that isotopic fractionation is reduced at high temperatures and ab initio modelling presented by Moynier et al. (2011) indicated that at magma ocean temperatures the difference in isotopic composition between spinel and silicates becomes too small to be resolvable at the current level of analytical precision. Another hypothesis to explain the similarity in Cr isotopes between low-Ti and high-Ti samples is a budget argument. The sources of these samples are mixtures of different sources (ultra-mafic minerals ± ilmenite and urKREEP) and Cr is likely to be depleted in some of these sources especially the urKREEP source due to its compatible behaviour during magmatic crystallisation. Ilmenite is only a minor Cr bearing phase, so the Cr measured in the different groups of sample is largely controlled by the Cr concentration in ultramafic minerals (pyroxene and spinel). Varying amounts of ilmenite will have limited effect on the Cr isotope composition of the source. However, further work on other lunar samples (e.g. other low-Ti suites and green glasses) will help to answer this question.

5.4. Implications for the formation of the Moon

Several models have explored the Giant Impact model and recent studies have argued that it may be possible to create the Earth-Moon system with both a small Mars-size impactor (Cuk and Stewart, 2012) and a similar size for the proto-Earth and the impactor (Canup, 2012). Although some of the samples analysed in this study have been affected by magmatic differentiation (Fig. 3a), we follow other studies (e.g. Warren and Taylor, 2014) and use the least differentiated mare basalts to assess the lunar mantle composition. Given the similarities in Cr isotopes between source regions of mare basalts, the least differentiated sample can be used to assess the lunar mantle composition. In the case of Cr isotopes, we use the least differentiated low-Ti mare basalts. Sample 12016 has been described in the literature as primary basalt (Hallis et al., 2010) and, as such, its Cr isotopic composition is the closest estimate of the Cr isotopic composition of the source rocks. In the case of low-Ti basalts, the source rock is believed to be a cumulate of ultramafic minerals (i.e. olivine and pyroxene, Beard et al., 1998). Our data suggest that there is no difference between the Cr isotopic composition of the lunar ($\delta^{53}\text{Cr} = -0.222 \pm 0.059\%$) and terrestrial ($\delta^{53}\text{Cr} = -0.124 \pm 0.101\%$, Schoenberg et al., 2008) mantles. This is an important observation and is consistent with other isotope systems (e.g. Wiechert et al., 2001; Liu et al., 2010). The similarity between Earth and Moon for $\delta^{53}\text{Cr}$ and $\varepsilon^{44}\text{Cr}$ could be explained by impact of a similar-sized body that experienced the same differentiation history and was derived from the same zone of the solar nebula. The homogeneity between the terrestrial and lunar mantles has other implications. Recent metal–silicate partition studies (Bonnand et al., 2016) indicate that Cr isotopic variations are unlikely to be produced during core formation, contrary to that proposed by Moynier et al. (2011), but consistent with the lack of difference between the BSE and chondritic meteorites (Bonnand et al., 2016). Therefore, our lunar Cr isotopic data does not resolve the chronology of when the Earth’s core formed relative to the Giant Impact, but does suggest that core formation on the Moon did not generated any significant Cr isotopic fractionation.

6. CONCLUSION

This study presents precise mass dependent stable Cr isotope data for 19 mare basalts. These samples are characterised by $\delta^{53}\text{Cr}$ values ranging from $-0.329\%e$ to $-0.147\%e$. The Cr isotopic compositions of mare basalts are positively correlated with Mg# which is an index of magmatic differentiation. Highly evolved lavas have the lightest $\delta^{53}\text{Cr}$ values. This fractionation is driven by crystallising phases enriched in Cr heavy isotopes. This is most likely Cr-spinel and chrome-rich ulvöspinel in the low-Ti basalts and chrome-rich ulvöspinel in the high-Ti basalts, both phases that contain octahedral co-ordinated Cr$^{3+}$. The presence of a phase containing Cr$^{3+}$ at the low oxygen fugacities found in the Moon (1–2 log units below IW) is favoured by low temperatures, which decreases the Cr$^{3+}$/Cr$^{4+}$ of melts and allows the spinel-saturation curve to be intersected. This explains the late crystallisation of chromium spinel in lunar basalts, which removes Cr$^{3+}$ from the melt and generates significant Cr isotopic fractionation.
The lack of differences between high-Ti and low-Ti basalt and between KREEP basalt and mare basalts suggest that the lunar mantle is relatively homogeneous in Cr isotopes. This also suggests that the LMO differentiation did not fractionate Cr isotopes. This may be due to higher temperatures during LMO differentiation compared to prevailing conditions during mare basalt differentiation.

Taking the sample that is thought to be closest in composition to a primary basalt as reflective of the isotopic composition of the lunar mantle indicates that there is no currently resolvable Cr isotope difference between the Moon and the bulk-silicate Earth. This similarity indicates that the Moon is formed mainly from Earth mantle material or by equilibration with Earth material. Using our current knowledge of meteoritic material this similarity in terrestrial and lunar mantle suggests core formation on the Moon (and on Earth) did not fractionate Cr isotopes further.

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APPENDIX A. SUPPLEMENTARY DATA

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.gca.2015.11.041.

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