



Open Research Online

The Open University's repository of research publications and other research outputs

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

Journal Item

How to cite:

Bonnand, Pierre; Parkinson, Ian J. and Anand, Mahesh (2016). Mass dependent fractionation of stable chromium isotopes in mare basalts: implications for the formation and differentiation of the Moon. *Geochimica et Cosmochimica Acta*, 175 pp. 208–221.

For guidance on citations see [FAQs](#).

© 2015 The Authors

Version: Version of Record

Link(s) to article on publisher's website:

<http://dx.doi.org/doi:10.1016/j.gca.2015.11.041>

Copyright and Moral Rights for the articles on this site are retained by the individual authors and/or other copyright owners. For more information on Open Research Online's data [policy](#) on reuse of materials please consult the policies page.

oro.open.ac.uk



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

Pierre Bonnand^{a,b,*}, Ian J. Parkinson^{a,c}, Mahesh Anand^{d,e}

^a Department of Environment, Earth and Ecosystems, The Open University, Walton Hall, Milton Keynes MK7 6AA, United Kingdom

^b Department of Earth Sciences, University of Oxford, South Parks Road, Oxford OX1 3AN, United Kingdom

^c School of Earth Sciences, University of Bristol, Wills Memorial Building, Queen's Road, Clifton BS8 1RJ, Bristol, United Kingdom

^d Department of Physical Sciences, The Open University, Walton Hall, Milton Keynes MK7 6AA, United Kingdom

^e Department of Earth Sciences, The Natural History Museum, London SW7 5DB, United Kingdom

Received 17 April 2015; accepted in revised form 11 November 2015; available online 12 December 2015

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 ($\delta^{53}\text{Cr}$) 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 $-0.222 \pm 0.025\%$, which is within error of the current BSE value ($-0.124 \pm 0.101\%$). 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.

© 2015 The Authors. Published by Elsevier Ltd. This is an open access article under the CC BY license (<http://creativecommons.org/licenses/by/4.0/>).

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;

* Corresponding author at: 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).

Chabot and Agee, 2003; Pahlevan, 2014; Dauphas et al., 2014). 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; Kruijjer 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; Armytage 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 (Taylor and Jakes, 1974; Snyder et al., 1992; Beard et al., 1998; Elardo et al., 2011; Elkins-Tanton et al., 2011; Elkins-Tanton and Bercovici, 2014). At the end of the LMO crystallisation a late residual liquid, enriched in incompatible elements (K, P, REE), termed urKREEP, crystallised (Warren and Wasson, 1979; Warren and Taylor, 2014). The timing and duration of LMO crystallisation has been intensively studied (e.g. Touboul et al., 2009; Muenker, 2010; Borg et al., 2011; Carlson et al., 2014) and could have occurred as early as 50 Ma after the formation of the Solar System, although this is still debated (e.g. Muenker, 2010). Nevertheless, differentiation of the LMO was most likely completed 200 Ma after the formation of the Solar System (e.g. Elkins-Tanton and Bercovici, 2014). The second phase of the lunar differentiation lasted from 3.9 Ga (after the period of heavy bombardment) to about 1.2 Ga (Hiesinger et al., 2010; Warren and Taylor, 2014) and evidence for this is the eruption of mare basalts on the surface of the Moon. Mare basalts are the product of partial melting of the ultramafic residue produced during the LMO differentiation. These basalts are Mg and Fe rich and have been split into three groups: very low-Ti ($\text{TiO}_2 < 1.5$ wt.%), low-Ti (1.5–6 wt.% TiO_2) and high-Ti

($\text{TiO}_2 > 6$ wt.%) (Neal and Taylor, 1992; Warren and Taylor, 2014).

Due to the lack of lunar mantle samples, mare basalts have been widely used to compare the chemical composition of the Moon with the Earth and other planets (e.g. Neal and Taylor, 1992). While a number of studies have investigated the chemical composition of mare basalts in order to constrain the events that occurred during the lunar differentiation and the timing of these events (e.g. Rhodes et al., 1977; Liu et al., 2010) more recently, elemental ratios have been used to constrain the chemical heterogeneity of the lunar mantle (e.g. Muenker, 2010). These studies have now been extended to stable isotopic compositions (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; Armytage 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. Fe (Poitrasson et al., 2004; Weyer et al., 2005; Liu et al., 2010) and Li (Magna et al., 2006) that have been interpreted in term of source heterogeneities, specifically the presence of ilmenite in the source of high-Ti basalts.

In this study we focus on the geochemistry of chromium (Cr) an element that has several geochemical properties that make it an ideal tool to investigate the formation of the Moon and its relationship to the Earth. Chromium is a moderately volatile element with a condensation temperature (T_c) of 1291 K, similar to Fe (1328 K) but significantly different to oxygen (180 K) (Lodders, 2003), two elements that have almost identical isotopic compositions for the Earth and Moon. Chromium is also a lithophile element but becomes siderophile at high temperature and pressure, and under more reduced conditions (Chabot and Agee, 2003). It is therefore depleted in the Earth's mantle relative to CI chondrite (e.g. Gessmann and Rubie, 2000) and this depletion is linked to the siderophile nature of Cr during core formation with ~60% of the Earth's Cr inventory thought to be in the core (Seifert and Ringwood, 1988; Allègre et al., 1995; McDonough, 2003). The lunar mantle is also depleted in Cr and V and this similarity has been used as an evidence for the chemical link between the two mantles (O'Neill, 1991; Gessmann and Rubie, 2000).

By contrast, the oxygen fugacity of the upper mantle of the Earth (Fayalite Magnetite Quartz (FMQ) ± 1 log units; Canil et al., 1994; Wood et al., 1990) is more oxidised than that of the lunar mantle (iron-wüstite (IW) -1 to -2 log units (or ~FMQ -5 to -6 log units); Wadhwa, 2008 and references therein). Therefore, in the terrestrial mantle chromium is mainly present as Cr^{3+} although it has also been suggested that small amounts of Cr^{2+} can be present (Papike et al., 2005) and spectroscopic studies indicate the presence of significant amounts of Cr^{2+} at high temperatures (1200–1400 °C) and terrestrial oxygen fugacities (FMQ ± 1), (Berry and O'Neill, 2004; Berry et al., 2006).

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 ($\sim 4000 \mu\text{g g}^{-1}$) compared to terrestrial basalts ($< 500 \mu\text{g g}^{-1}$; Basaltic Volcanism Study Project, 1981) could be due to the fact that Cr is less compatible under low $f\text{O}_2$ 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}Mn to ^{53}Cr (half-life 3.7 Ma) and/or production of the neutron-rich isotope ^{54}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}Mn , or that both the impactor and the proto-Earth had similar Mn/Cr ratios and ^{53}Mn abundance. Similarly the lack of difference in $^{54}\text{Cr}/^{52}\text{Cr}$ ratios suggests a similar 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 δ notation relative to NBS979 chromium standard ($\delta^{53}\text{Cr} = ((^{53}\text{Cr}/^{52}\text{Cr}_{\text{sample}} / ^{53}\text{Cr}/^{52}\text{Cr}_{\text{NBS979}} - 1) \times 1000)$) (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 ($\delta^{53}\text{Cr} = -0.124\text{‰} \pm 0.101$, 2 s.d., $n = 24$, Fig. 1) 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

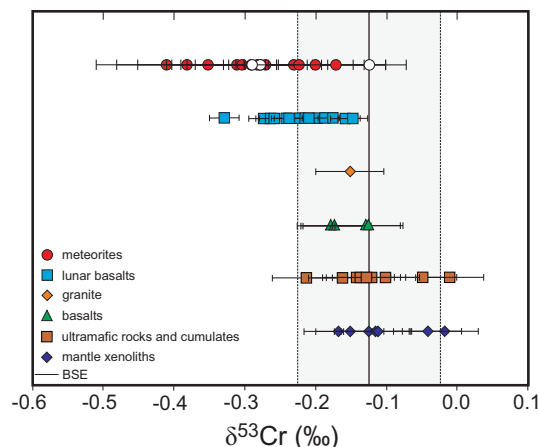


Fig. 1. Compilation of Cr isotopes data from the literature together with the data presented in this study. Data for granite, basalts and ultramafic rocks and cumulates are from Schoenberg et al. (2008). The meteorites data are from Moynier et al. (2011) (full circles) and Schiller et al. (2014) (open circles). The lunar data are from this study. The grey vertical bar defines the estimated range for the BSE value ($-0.124 \pm 0.101\text{‰}$, Schoenberg et al., 2008).

(Qin et al., 2015; Bonnand et al., 2016; Schoenberg et al., 2015). The contrasting results of these studies may be related to analytical artefacts from the standard-bracketing technique (Bonnand et al., 2016). Moreover, metal–silicate partitioning experiments suggest there is no Cr isotope fractionation during core formation (Bonnand et al., 2016) supporting the observation that meteorites and Earth’s mantle have the same stable Cr isotope composition.

In this study we present the first mass-dependent Cr isotope data for lunar basalts utilising a double-spike technique. We address whether the similarities in mass independent Cr isotopes extend to mass dependent Cr isotopes, assess whether any stable Cr isotope heterogeneities exist in the source regions of low- and high-Ti mare basalts and explore the sensitivity of Cr isotope fractionation to the contrasting redox states of the lunar and terrestrial mantles. This study also builds on our knowledge of utilising stable Cr isotopes as a tool to interrogate planetary formation and differentiation.

2. SAMPLES

The samples investigated in this study have previously been analysed for major and trace element concentrations and for their O isotopes (Hallis et al., 2010, 2014). The samples are representative of the most abundant types of mare basalt. They comprise ten low-Ti, eight high-Ti basalts and one “KREEP” basalt (Table 1). Detailed petrography, mineralogy and major and trace element data for these samples are available in the lunar sample compendium (Meyer, 2004–2011) and in Hallis et al. (2010; 2014). The low-Ti basalts analysed in this study were collected during the Apollo 12, 14 and 15 missions. Apollo 12 basalts are subdivided into three subgroups: olivine basalt (12040), ilmenite

Table 1

Cr isotopic composition of mare basalts analysed in this study together with other geochemical data. Cr, Ti, Mg and Fe concentration are from [Hallis et al. \(2014\)](#). The 2 s.d. is the standard deviation on the JP-1 peridotite standard (see text for details and [electronic annex table](#)).

| Apollo mission | Sample number | Sample Type | $\delta^{53}\text{Cr}$ ‰ | 2 s.d. ‰ | Cr $\mu\text{g g}^{-1}$ | TiO ₂ wt.% | MgO wt.% | FeO wt.% | Mg# |
|-----------------|---------------|--------------|--------------------------|----------|-------------------------|-----------------------|----------|----------|------|
| | JP-1 | Peridotite | −0.128 | 0.022 | | | | | |
| 11 | 10017 | High-Ti | −0.216 | 0.022 | 2330 | 11.72 | 7.15 | 20.18 | 40.9 |
| | 10050 | High-Ti | −0.263 | 0.022 | 2250 | 11.68 | 7.74 | 19.08 | 42.8 |
| | 10057 | High-Ti | −0.211 | 0.022 | 2190 | 11.27 | 7.47 | 20.24 | 40.2 |
| | 10058 | High-Ti | −0.274 | 0.022 | 1410 | 8.66 | 6.11 | 18.46 | 41.1 |
| | 10072 | High-Ti | −0.271 | 0.022 | 2390 | 11.89 | 7.61 | 20.03 | 37.6 |
| 17 | 70017 | High-Ti | −0.178 | 0.022 | 3700 | 13.38 | 9.64 | 19.18 | 48.7 |
| | 70035 | High-Ti | −0.257 | 0.022 | 3530 | 13.73 | 9.31 | 21.32 | 44.7 |
| | 70215 | High-Ti | −0.218 | 0.022 | 2680 | 13.32 | 8.61 | 20.63 | 44.2 |
| | 74275 | High-Ti | −0.227 | 0.022 | 3830 | 12.74 | 10.1 | 18.53 | 50.1 |
| | 75055 | High-Ti | −0.171 | 0.022 | 2570 | 12.91 | 8.13 | 16.45 | 45.8 |
| Average high-Ti | | | −0.229 | 0.074 | | | | | |
| 12 | 12016 | 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 | 20.56 | 41.0 |
| | 12064 | Low-Ti | −0.242 | 0.022 | 1950 | 3.66 | 6.37 | 19.51 | 37.9 |
| 14 | 14053 | Low-Ti | −0.238 | 0.022 | 2100 | 2.60 | 7.81 | 16.88 | 46.6 |
| 15 | 15016 | 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 low-Ti | | | −0.215 | 0.058 | | | | | |

basalt (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 TiO₂ 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 ([Baldrige 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 resolvable difference in mass independent Cr isotopes between the Moon and Earth (see introduction) the stable Cr isotope 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 HNO₃-HF-HCl acid mixtures. The fully dissolved sample was evaporated to dryness and

then re-dissolved in 6 M HCl. An aliquot of $\sim 1 \mu\text{g}$ of chromium was spiked with a requisite amount of ^{50}Cr – ^{54}Cr double spike ([Bonnand et al., 2011](#)) and the solutions were then dried down and taken up again in 6 M HCl to ensure equilibration 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 HNO₃. A disposable Bio-Rad Poly-Prep column was filled with 1 mL of cationic AG50 X8 200–400 mesh resin. The resin was first cleaned with 20 ml 6 M HCl and 20 ml MQ H₂O and then preconditioned with 10 ml of 0.5 M HNO₃. The sample was then loaded in 4 ml 0.5 M HNO₃. In a weak HNO₃ medium, Cr³⁺ will stick to the cation resin. The column is then washed with 4 ml 0.5 M HNO₃, then 6 ml 0.5 M HNO₃ + 0.25 M HF, then 7 ml 0.5 M HCl. Finally, the clean 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 use of the double spike method allows for the correction of isotope fractionation during chemical separation. The total blank of this

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 ($\Delta M/M > 5500$), which ensures that polybaric interferences are resolved from the isotopes of interest. Potential isobaric interferences from Fe, Ti and V were monitored on masses ^{56}Fe , ^{49}Ti and ^{51}V , and ^{54}Cr and ^{50}Cr signals were corrected for isobaric contributions, although these corrections were always negligible and within the internal uncertainty of the $\delta^{53}\text{Cr}$ measurements. An instrumental ‘on-mass’ background was determined by measuring the same 0.3 M HNO_3 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 $\delta^{53}\text{Cr}$ values obtained from these experiments are $\delta^{53}\text{Cr} = -0.003 \pm 0.011\text{‰}$ (2 standard deviation, $n = 4$). The reproducibility of the mass spectrometer analyses was assessed with multiple measurements of a spiked NBS SRM 979 solution ($\delta^{53}\text{Cr} = 0.000 \pm 0.014\text{‰}$, 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 $-0.128 \pm 0.022\text{‰}$ (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 $\delta^{53}\text{Cr}$ values within 0.4‰ of NBS SRM 979, the choice of fractionation law produces minimal additional uncertainty ($\sim 0.004\text{‰}$). 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 $\delta^{53}\text{Cr}$ which are expected in silicate samples (Schoenberg et al., 2008; Farkaš 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 $\mu\text{g g}^{-1}$ (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 TiO_2 concentration.

The Cr isotopic compositions of lunar samples analysed in this study are reported in Table 1 together with other

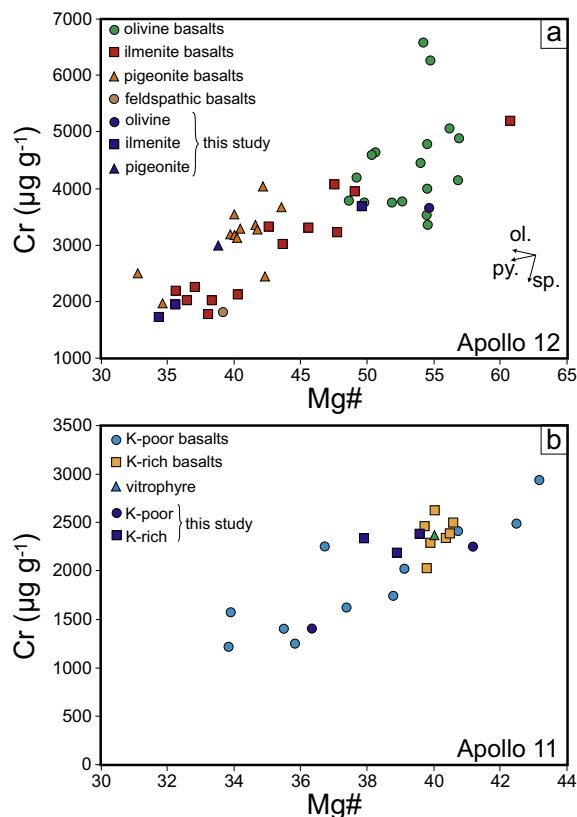


Fig. 2. Compilation of Cr concentration versus Mg# in Apollo 12 (a) and Apollo 11 (b) mare basalts. Data are from Rhodes and Blanchard (1980), Compston et al. (1970), Goles et al. (1970), Beatty et al. (1979), Duncan et al. (1976), Willis et al. (1972), Rhodes et al. (1977), Rhodes et al. (1976), Warner et al. (1979), Grove and Beatty (1980), Compston et al. (1971), Neal et al. (1994), Snyder et al. (1997) and Kushiro and Haramura (1971).

geochemical data. Lunar samples are characterised by relatively small variation in $\delta^{53}\text{Cr}$ from -0.329 to -0.147% (Fig. 1), but overall, lunar samples are characterised by lighter $\delta^{53}\text{Cr}$ compared to the bulk-silicate Earth ($-0.124 \pm 0.101\%$, Schoenberg et al., 2008), and double spike data for meteorites (Bonnard et al., 2016), although there is some clear overlap in composition. Nevertheless, the lunar samples have slightly more positive $\delta^{53}\text{Cr}$ than the chondritic meteorite data of Moynier et al. (2011) and Schiller et al. (2014) (Fig. 1). Chromium isotopes in all the lunar basalts analysed in this study show a weak positive correlation with Mg# and Cr concentrations (Fig. 3). However, in

detail there is a broad negative correlation between Cr isotopic composition and TiO_2 in low-Ti samples, that is statistically significant when only the Apollo 12 samples are considered ($r^2 = 0.95$, $n = 5$). By contrast the high-Ti samples have a weak positive correlation between $\delta^{53}\text{Cr}$ and TiO_2 . Given our uncertainty and the range of $\delta^{53}\text{Cr}$ values in both high-Ti and low-Ti samples, there is no clear distinction between low-Ti and high-Ti basalts (Fig. 3c) particularly when the most primitive samples are considered from each suite. This observation is different to findings for other isotopic systems such as Fe and O (Weyer et al., 2005; Spicuzza et al., 2007; Liu et al., 2010), where distinct differences exist between these two groups. In fact there is no correlation between Cr isotopes and O isotopes in the lunar samples analysed here. The KREEP sample (15386) analysed in this study has an isotopic composition similar to the least fractionated mare basalt (Fig. 3). The olivine cumulate sample (12040, Baldrige et al., 1979) is characterised by the heaviest Cr isotopic composition measured for the lunar samples, whereas the low-Ti sample 12051, characterised by the lowest Mg#, also has the lightest Cr isotopic composition for the lunar samples measured in this study. There is also a weak positive correlation between Cr concentration and Cr isotopes in our lunar dataset (Fig. 3b), but no correlation between Cr isotopes and the modal abundance of key minerals such as olivine and pyroxene, nor any obvious correlation with Al_2O_3 or any other major elements (not shown).

5. DISCUSSION

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.

5.1. Chromium concentration in lunar basalts

The Cr concentrations in mare basalts range from $1410 \mu\text{g g}^{-1}$ to $6075 \mu\text{g g}^{-1}$ which is higher than the average Cr concentration in primitive terrestrial basalts ($\sim 500 \mu\text{g g}^{-1}$, 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 $f\text{O}_2$ (IW-2) present in the Moon, Cr^{2+} will be the dominant species of Cr, with $\text{Cr}^{2+}/\text{Cr}_{\text{TOT}}$ ratios of ~ 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

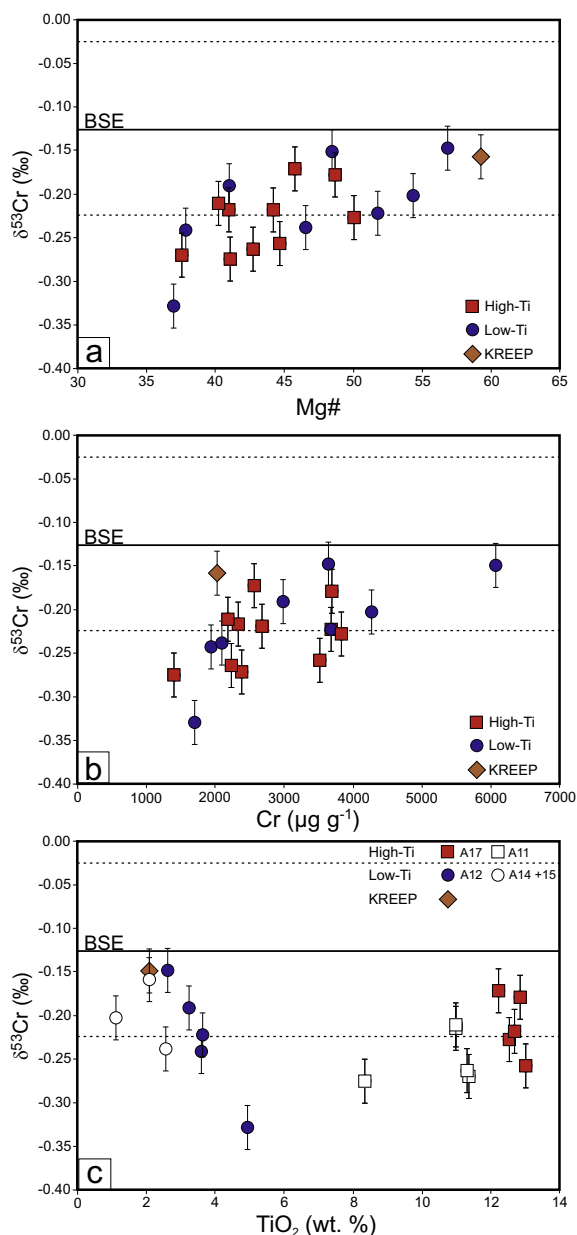


Fig. 3. Cr isotopic composition versus Mg# (a), Cr concentration (b) and TiO_2 (c) in mare basalts analysed in this study. The BSE value is from Schoenberg et al. (2008), (solid line is the mean and dotted line is ± 2 s.d.; see text for details).

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 $\text{Cr}^{2+}/\text{Cr}^{3+}$ 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 $\text{Cr}^{2+}/\text{Cr}^{3+}$ ratios (Schreiber and Haskin, 1976; Berry et al., 2006) also lowering the spinel-saturation concentration to below $700 \mu\text{g g}^{-1}$ (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 basalts. 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 basalts 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 $4000 \mu\text{g g}^{-1}$ to about $5500 \mu\text{g g}^{-1}$ 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_{Cr} in spinel = 50 and D_{Cr} 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 incompatible element and so the spinel phase must be a low-Ti chromium spinel ($\text{TiO}_2 < 10 \text{ wt. } \%$), 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 $\text{Cr}^{2+}/\text{Cr}_{\text{TOT}}$ ratio is 0.6–0.7, so that for lavas with $2500\text{--}3000 \mu\text{g g}^{-1}$ Cr, the amount of Cr^{3+} is high enough ($\sim 700 \mu\text{g g}^{-1}$, 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 $\sim 1150 \text{ }^\circ\text{C}$ (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 $1500\text{--}2000 \mu\text{g g}^{-1}$ 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

Table 2

Mineral composition of low-Ti mare basalt 12016. Mineral chemical composition is from [Dungan and Brown \(1977\)](#). Modal abundances are from [Hallis et al. \(2010\)](#). The partition coefficients are from [Seifert and Ringwood \(1988\)](#).

| Mineral | Olivine | Pyroxene | Spinel | Feldspar | Ilmenite |
|--------------------------------|---------|----------|--------|----------|----------|
| SiO ₂ | 36.62 | 49.72 | n.d. | 46.75 | n.d. |
| TiO ₂ | 0.05 | 1.66 | 8.68 | 0.09 | 52.90 |
| Al ₂ O ₃ | 0.00 | 3.38 | 11.29 | 33.59 | n.d. |
| Cr ₂ O ₃ | 0.13 | 0.89 | 40.26 | n.d. | 0.50 |
| FeO | 29.02 | 13.18 | 35.46 | 0.49 | 44.50 |
| MnO | 0.34 | 0.26 | 0.52 | n.d. | n.d. |
| MgO | 32.92 | 16.27 | 3.63 | 0.30 | 1.20 |
| CaO | 0.25 | 13.84 | 0.05 | 17.39 | n.d. |
| Na ₂ O | n.d. | 0.06 | n.d. | 0.97 | n.d. |
| K ₂ O | n.d. | n.d. | n.d. | 0.06 | n.d. |
| BaO | n.d. | n.d. | n.d. | 0.00 | n.d. |
| Total | 99.33 | 99.26 | 99.89 | 99.60 | 99.10 |
| Modal ab. | 12 | 52.1 | 1.6 | 29.1 | 4.8 |
| % of total Cr | 1.4 | 40.4 | 56.1 | 0.0 | 2.1 |
| Cr Kd min./melt | 0.8 | 2.5 | 50 | 0.0001 | ? |

by pyroxene crystallisation alone, but also requires the stabilisation of Cr³⁺ 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 Cr³⁺ to Cr²⁺ ([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 Cr²⁺/Cr_{TOT} 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 δ⁵³Cr 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, Δ⁵³Cr, 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 Δ⁵³Cr is small (<-0.1‰, [Fig. 5b](#)). If the Δ⁵³Cr was fixed to -0.05 then pyroxene followed by pyroxene + spinel crystallisation can explain the light δ⁵³Cr in the evolved Apollo 12 samples ([Fig. 5b](#)). Much of the fractionation can be accommodated by <1% spinel fractionation with a Δ⁵³Cr of -0.15 ([Fig. 5c](#)), a value more consistent with the data of [Moynier et al. \(2011\)](#), if the spinel removes the majority of Cr³⁺. Similarly, light δ⁵³Cr is found in high-Ti lavas through crystallisation of Cr-rich ulvöspinel although the Cr-δ⁵³Cr systematics are less obvious because Cr-rich ulvöspinel 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

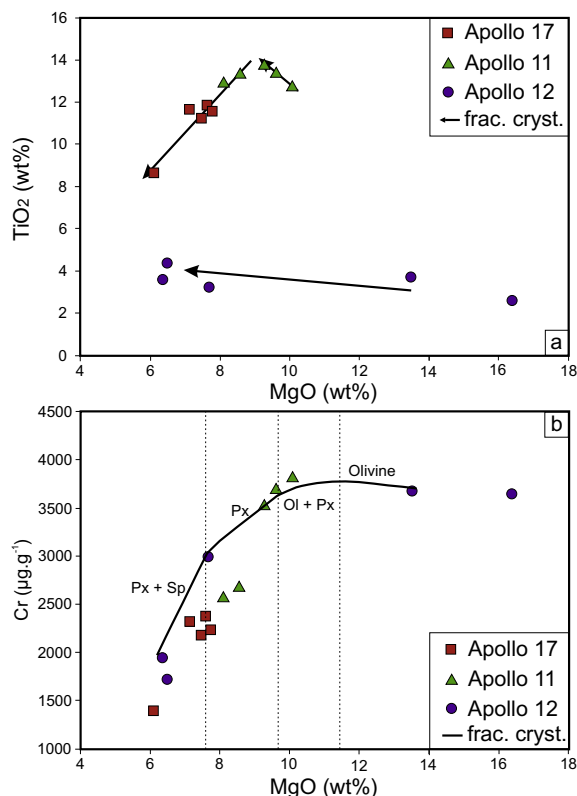


Fig. 4. TiO_2 concentration (a) and Cr concentration (b) versus MgO concentration for Apollo 11, 12 and 17 samples analysed in this study. The concentration data is from Hallis et al. (2014). The black arrows in (a) show the chemical evolution during fractional crystallisation indicating the high-Ti 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).

that the data are consistent with crystallisation of a Cr-rich phase with a heavy $\delta^{53}\text{Cr}$ 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

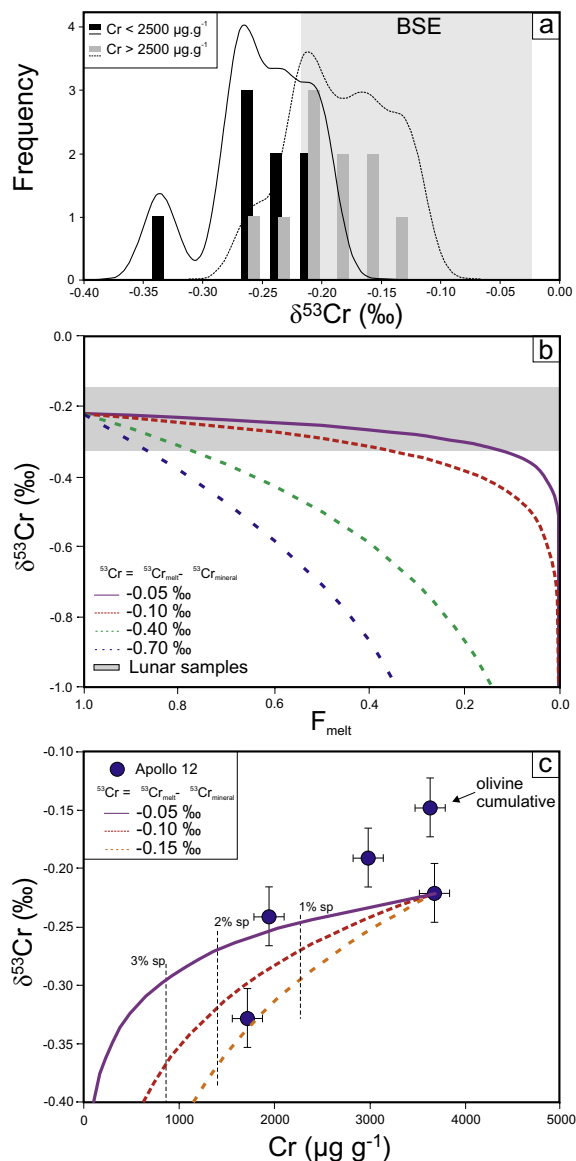


Fig. 5. (a) Histogram and calculated cumulative frequency of $\delta^{53}\text{Cr}$ values for low-Ti and high-Ti basalts analysed in this study. The two groups of samples were selected based on their Cr concentration (<2500 or >2500 $\mu\text{g g}^{-1}$, see text for details). The vertical grey bar 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 $\Delta^{53}\text{Cr}$ ($\delta^{53}\text{Cr}_{\text{melt}} - \delta^{53}\text{Cr}_{\text{mineral}}$) values used in the calculation. (c) Plot of Apollo 12 mare basalts and are Rayleigh fractionation models during fractional crystallisation assuming $\Delta^{53}\text{Cr} = -0.05\text{‰}$, -0.1‰ and -0.15‰ . The lines are labelled with the proportion of Cr-spinel crystallised. The $\delta^{53}\text{Cr}$ of the melt ($\delta^{53}\text{Cr}_{\text{melt}}$) is calculated using $\delta^{53}\text{Cr}_{\text{melt}} = (\delta^{53}\text{Cr}_{\text{initial}} + 1000) * F_{\text{melt}}^{(f-1)} - 1000$ where $\delta^{53}\text{Cr}_{\text{initial}}$ is the initial stable Cr isotope composition and F_{melt} is the fraction of Cr remaining in the melt.

the melt. Further experimental work is required to unravel which mechanism is the most likely.

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 $-0.215 \pm 0.058\text{‰}$ and $-0.229 \pm 0.074\text{‰}$ 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 its 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 \pm 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 basalt. 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 ($\delta^{53}\text{Cr} = -0.222 \pm 0.050\text{‰}$) and terrestrial ($\delta^{53}\text{Cr} = -0.124\text{‰} \pm 0.101$, 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 in lunar and terrestrial Si isotopes has been used to constrain the models proposed for the Giant Impact and the formation of the Earth's satellite (Pahlevan and Stevenson, 2007). The similarity between Earth and Moon for $\delta^{53}\text{Cr}$ and $\epsilon^{54}\text{Cr}$ 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 generate 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‰ to -0.147‰ . 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 $\text{Cr}^{2+}/\text{Cr}^{3+}$ 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 suggest core formation on the Moon (and on Earth) did not fractionate Cr isotopes further.

ACKNOWLEDGEMENTS

Research funding for this work was provided by The Open University to IJP and by UK Science and Technology Facilities Council (STFC) grants to M.A. (grant nos. ST/I001298/1 & ST/L000776/1). We thank Manuela Fehr for her help using the Open University MC-ICP-MS instrument. The authors would like to thank Alex Halliday and Jon Wade for their constructive comments on an earlier version of this manuscript. We would like to thank F. Poitrasson and two anonymous reviewers for their useful comments that helped to improve the manuscript.

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>.

REFERENCES

- Allègre C. J., Poirier J. P., Humler E. and Hofmann A. W. (1995) The chemical-composition of the Earth. *Earth Planet. Sci. Lett.* **134**, 515–526.
- Armytage R. M. G., Georg R. B., Williams H. M. and Halliday A. N. (2012) Silicon isotopes in lunar rocks: implications for the Moon's formation and the early history of the Earth. *Geochim. Cosmochim. Acta* **77**, 504–514.
- Baldrige W. S., Beatty D. W., Hill S. M. R. and Albee A. L. (1979) The petrology of the Apollo 12 pigeonite basalt suite. *Proc. Lunar Planet. Sci. Conf.* **10**, 141–179.
- Ball J. W. and Izbicki J. A. (2004) Occurrence of hexavalent chromium in ground water in the western Mojave Desert, California. *Appl. Geochem.* **19**, 1123–1135.
- Ballhaus C., Berry R. F. and Green D. H. (1991) High pressure experimental calibration of the olivine-orthopyroxene-spinel oxygen barometer: implications for the oxidation state of the mantle. *Contrib. Mineral. Petrol.* **107**, 27–40.
- Beard B. L., Taylor L. A., Scherer E. E., Johnson C. M. and Snyder G. A. (1998) The source region and melting mineralogy of high-titanium and low-titanium lunar basalts deduced from Lu-Hf isotope data. *Geochim. Cosmochim. Acta* **62**, 525–544.
- Beatty D. W., Hill S. M. R. and Albee A. L., et al. (1979) Apollo 12 feldspathic basalts 12031, 12038 and 12072: petrology, comparison and interpretations. *Lunar Planet. Sci. Conf. Proc.* **10**, 115–139.
- Berry A. J., O'Neill H. and St C. (2004) A XANES determination of the oxidation state of chromium in silicate glasses. *Am. Mineral.* **89**, 790–798.
- Berry A. J., O'Neill H., St C., Scott D. R., Foran G. J. and Shelley J. M. G. (2006) The effect of composition on Cr²⁺/Cr³⁺ in silicate melts. *Am. Mineral.* **91**, 1901–1908.
- Birck J. L. and Allègre C. J. (1988) Manganese chromium isotope systematics and the development of the early solar-system. *Nature* **331**, 579–584.
- Bonnand P., Parkinson I. J., James R. H., Karjalainen A.-M. and Fehr M. A. (2011) Accurate and precise determination of stable Cr isotope compositions in carbonates by double spike MC-ICP-MS. *J. Anal. Atom. Spectrom.* **26**, 528–535.
- Bonnand P., James R. H., Parkinson I. J., Connelly D. P. and Fairchild I. J. (2013) The chromium isotopic composition of seawater and marine carbonates. *Earth Planet. Sci. Lett.* **382**, 10–20.
- Bonnand P., Williams H. M., Parkinson I. J., Wood B. J. and Halliday A. N. (2016) Stable chromium isotopic composition of meteorites and metal-silicate experiments: Implications for fractionation during core formation. *Earth Planet. Sci. Lett.* **3**, 4–7. <http://dx.doi.org/10.1016/j.epsl.2015.11.026>.
- Borg L. E., Connelly J. N., Boyet M. and Carlson R. W. (2011) Chronologic evidence that the Moon is either young or did not have a global magma ocean. *Nature* **477**, 70–72.
- Cameron A. and Ward W. (1976) The origin of the Moon. *Proc. Lunar Planet. Sci. Conf.*, 120–122.
- Canil D., O'Neill H. S., Pearson D. G., Rudnick R. L., McDonough W. F. and Carswell D. A. (1994) Ferric iron in peridotites and mantle oxidation states. *Earth Planet. Sci. Lett.* **123**, 205–220.
- Canup R. M. (2004) Simulations of a late lunar-forming impact. *Icar* **168**, 433–456.
- Canup R. M. (2012) Forming a Moon with an Earth-like composition via a giant impact. *Science* **338**, 1052–1055.
- Carlson R. W., Borg L. E., Gaffney A. M. and Boyet M. (2014) Rb-Sr, Sm-Nd and Lu-Hf isotope systematics of the lunar Mg-suite: refining the age and duration of lunar crust formation. *Phil. Trans. R. Soc. A* **372**(2024), 20130246.
- Caro G. (2011) Early Silicate Earth Differentiation. In (eds. R. Jeanloz, K. H. Freeman). *Ann. Rev. Earth. Planet. Sci.*, 39, pp. 31–58.
- Chabot N. L. and Agee C. B. (2003) Core formation in the Earth and Moon: new experimental constraints from V, Cr, and Mn. *Geochim. Cosmochim. Acta* **67**, 2077–2091.
- Chappell B. W. and Green D. H. (1973) Chemical compositions and petrogenetic relationships in Apollo-15 mare basalts. *Earth Planet. Sci. Lett.* **18**, 237–246.
- Compston W., Chappell B. W. and Arriens P. A., et al. (1970) The chemistry and age of Apollo 11 lunar material. *Proc. 1st Lunar Sci. Conf.*, 1007–1027.
- Compston W., Berry H. and Vernon M. J., et al. (1971) Rubidium-strontium chronology and chemistry of lunar material from the Ocean of Storms. *2nd Lunar Sci. Conf.*, 1471–1485.
- Cuk M. and Stewart S. T. (2012) Making the Moon from a fast-spinning Earth: a giant impact followed by resonant despinning. *Science* **338**, 1047–1052.
- Dauphas N., Burkhardt C., Warren P. H. and Teng F. Z. (2014) Geochemical arguments for an Earth-like Moon-forming impactor. *Phil. Trans. R. Soc. A* **372**(2024), 20130244.

- Day J. M. D. and Moynier F. (2014) Evaporative fractionation of volatile stable isotopes and their bearing on the origin of the Moon. *Phil. Trans. R. Soc. A* **372**(2024), 20130259.
- Delano J. W. (1979) Apollo 15 green glass: chemistry and possible origin. *Geochim. et Cosmochim. Acta 10th Lunar Sci. Conf.* **1** (Suppl. 11), 275–300.
- Duncan A. R., Sher M. K. and Abraham Y. C., et al. (1976) Source region constraints for lunar basalt types inferred from trace element chemistry. *6th Lunar Sci. Conf.*, 218–220.
- Dungan M. A. and Brown R. W. (1977) The petrology of the Apollo 12 ilmenite basalt suite. *8th Lunar Sci. Conf.*, 1339–1381.
- El Goresy A., Ramdohr P. and Taylor L. A. (1971) The geochemistry of opaque minerals in Apollo 14 crystalline rocks. *Earth Planet. Sci. Lett.* **13**, 121–129.
- Elardo S. M., Draper D. S. and Shearer C. K. (2011) Lunar Magma Ocean crystallization revisited: bulk composition, early cumulate mineralogy, and the source regions of the highlands Mg-suite. *Geochim. Cosmochim. Acta* **75**, 3024–3045.
- Elkins-Tanton L. T. and Bercovici D. (2014) Contraction or expansion of the Moon's crust during magma ocean freezing? *Phil. Trans. R. Soc. A* **372**(2024), 20130240.
- Elkins-Tanton L. T., Burgess S. and Yin Q.-Z. (2011) The lunar magma ocean: reconciling the solidification process with lunar petrology and geochronology. *Earth Planet. Sci. Lett.* **304**, 326–336.
- Ellis A. S., Johnson T. M. and Bullen T. D. (2002) Chromium isotopes and the fate of hexavalent chromium in the environment. *Science* **295**, 2060–2062.
- Farkaš J., Chrástný V., Novák M., Čadkova E., Pašava J., Chakrabarti R., Jacobsen S. B., Ackerman L. and Bullen T. D. (2013) Chromium isotope variations ($\delta^{53/52}\text{Cr}$) in mantle-derived sources and their weathering products: Implications for environmental studies and the evolution of $\delta^{53/52}\text{Cr}$ in the Earth's mantle over geologic time. *Geochim. Cosmochim. Acta* **123**, 74–92.
- Gessmann C. K. and Rubie D. C. (2000) The origin of the depletions of V, Cr and Mn in the mantles of the Earth and Moon. *Earth Planet. Sci. Lett.* **184**, 95–107.
- Goles G., Randle K. and Osawa M., et al. (1970) Elemental abundances by instrumental activation analyses in chips from 27 lunar rocks. *1st Lunar Sci. Conf.*, 1165–1176.
- Grove T. L. and Beatty D. W. (1980) Classification, experimental petrology and possible volcanic histories of the Apollo 11 high K basalts. *Proc. Lunar Planet. Sci. Conf.* **11**, 149–177.
- Haggerty S. E. and Meyer H. O. A. (1970) Apollo 12: opaque oxides. *Earth Planet. Sci. Lett.* **5**, 379–387.
- Hallis L. J. (2010) The Geology of the Moon: Geochemistry and Petrology of Lunar Basalts. (Ph.D. thesis). The Open University.
- Hallis L. J., Anand M., Greenwood R. C., Miller M. F., Franchi I. A. and Russell S. S. (2010) The oxygen isotope composition, petrology and geochemistry of mare basalts: evidence for large-scale compositional variation in the lunar mantle. *Geochim. Cosmochim. Acta* **74**, 6885–6899.
- Hallis L. J., Anand M. and Strekopytov S. (2014) Trace-element modelling of mare basalt parental melts: implications for a heterogeneous lunar mantle. *Geochim. Cosmochim. Acta* **134**, 289–316.
- Hanson B. and Jones J. H. (1998) The systematics of Cr^{3+} and Cr^{2+} partitioning between olivine and liquid in the presence of spinel. *Am. Mineral.* **83**, 669–684.
- Hartmann W. K. and Davis D. R. (1975) Satellite-sized planetesimals and lunar origin. *Icaris* **24**, 504–515.
- Hauri E. H., Saal A. E., Rutherford M. J. and Orman J. A. (2015) Water in the Moon's interior: truth and consequences. *Earth Planet. Sci. Lett.* **409**, 252–264.
- Herwartz D., Pack A., Friedrichs B. and Bischoff A. (2014) Identification of the giant impactor Theia in lunar rocks. *Science* **344**, 1146–1150.
- Hiesinger H., Head J. W., Wolf U., Jaumann R. and Neukum G. (2010) Ages and stratigraphy of lunar mare basalts in Mare Frigoris and other nearside maria based on crater size-frequency distribution measurements. *J. Geophys. Res.* **115**, 2156–2202.
- Kamenetsky V. S., Crawford A. J. and Meffre S. (2001) Factors controlling chemistry of magmatic spinel: an empirical study of associated ultramafic rocks of the Iti and Kallidromon ophiolites (Central Greece). *Lithos* **99**, 136–149.
- Kinzler R. J. and Grove T. L. (1992) Primary magmas of mid-ocean ridge basalts 1. Experiments and methods. *J. Geophys. Res.* **97**, 6885–6906.
- Krujer T. S., Kleine T., Fisher-Godde M. and Sprung P. (2015) Lunar tungsten isotopic evidence for the late veneer. *Nature*. <http://dx.doi.org/10.1038/nature14360>.
- Kushiro I. and Haramura H. (1971) Major element variation and possible source materials of Apollo-12 crystalline rocks. *Science* **171**, 1235–1239.
- Li J.-P., O'Neill H., St C. and Seifert F. (1995) Subsolidus phase relations in the system $\text{MgO-SiO}_2\text{-Cr-O}$ in equilibrium with metallic Cr, and their significance for the petrochemistry of chromium. *J. Petrol.* **36**, 107–132.
- Liu Y., Spicuzza M. J., Craddock P. R., Day J. M. D., Valley J. W., Dauphas N. and Taylor L. A. (2010) Oxygen and iron isotope constraints on near-surface fractionation effects and the composition of lunar mare basalt source regions. *Geochim. Cosmochim. Acta* **74**, 6249–6262.
- Lodders K. (2003) Solar system abundances and condensation temperatures of the elements. *Astrophys. J.* **591**, 1220–1247.
- Longhi J. (1987) On the connection between mare basalts and picritic volcanic glasses. *J. Geophys. Res.* **92**, 349–360.
- Longhi J. (1992) Experimental petrology and petrogenesis of mare volcanics. *Geochim. Cosmochim. Acta* **56**, 2235–2251.
- Lugmair G. W. and Shukolyukov A. (1998) Early Solar system timescales according to Mn-53–Cr-53 systematics. *Geochim. Cosmochim. Acta* **62**, 2863–2886.
- Magna T., Wiechert U. and Halliday A. N. (2006) New constraints on the lithium isotope compositions of the Moon and terrestrial planets. *Earth Planet. Sci. Lett.* **243**, 336–353.
- Mastrobuono-Battisti A., Perets H. B. and Raymond S. N. (2015) A primordial origin for the compositional similarity between the Earth and the Moon. *Nature* **520**, 212–215.
- McDonough W. F. (2003) Compositional model for the Earth's core. In *Treatise on Geochemistry: The Mantle and Core*, vol. 2 (eds. R. W. Carlson, H. D. Holland and K. K. Turekian). Elsevier, Oxford, pp. 547–569.
- Moynier F., Albarede F. and Herzog G. F. (2006) Isotopic composition of zinc, copper, and iron in lunar samples. *Geochim. Cosmochim. Acta* **70**, 6103–6117.
- Moynier F., Yin Q.-Z. and Jacobsen B. (2007) Dating the first stage of planet formation. *Astrophys. J.* **671**, 181–183.
- Moynier F., Yin Q.-Z. and Schauble E. (2011) Isotopic evidence of Cr partitioning into Earth's core. *Science* **331**, 1417–1420.
- Muenker C. (2010) A high field strength element perspective on early lunar differentiation. *Geochim. Cosmochim. Acta* **74**, 7340–7361.
- Neal C. R. and Taylor L. A. (1992) Petrogenesis of mare basalts: a record of lunar volcanism. *Geochim. Cosmochim. Acta* **56**, 2177–2211.

- Neal C. R., Hacker M. D., Snyder G. A., Taylor L. A., Liu Y. G. and Schmitt R. A. (1994) Basalt generation at the Apollo 12 site I. New data, classification and reevaluation. *Meteoritics* **9**, 334–348.
- O'Neill H. St. (1991) The origin of the moon and the early history of the Earth-A chemical model I-The Moon. *Geochim. Cosmochim. Acta* **55**, 1135–1157.
- Pahlevan K. (2014) Isotopes as tracers of the sources of the lunar material and processes of lunar origin. *Phil. Trans. A R. Soc.* **372**(2024), 20130257.
- Pahlevan K. and Stevenson D. J. (2007) Equilibration in the aftermath of the lunar-forming giant impact. *Earth Planet. Sci. Lett.* **262**, 438–449.
- Paniello R. C., Day J. M. D. and Moynier F. (2012) Zinc isotopic evidence for the origin of the Moon. *Nature* **490**, 376–379.
- Papike J. J., Hodges F. N., Bence A. E., Cameron M. and Rhodes J. M. (1976) Mare basalts: crystal chemistry, mineralogy, and petrology. *Rev. Geophys. Space Phys.* **14**, 475–540.
- Papike J. J., Karner J. M. and Shearer C. K. (2005) Comparative planetary mineralogy: valence state partitioning of Cr, Fe, Ti, and V among crystallographic sites in olivine, pyroxene, and spinel from planetary basalts. *Am. Mineral.* **90**, 277–290.
- Poitrasson F., Halliday A. N., Lee D. C., Levasseur S. and Teutsch N. (2004) Iron isotope differences between Earth, Moon, Mars and Vesta as possible records of contrasted accretion mechanisms. *Earth Planet. Sci. Lett.* **223**, 253–266.
- Qin L., Alexander C. M. O. D., Carlson R. W., Horan M. F. and Yokoyama T. (2010) Contributors to chromium isotope variation of meteorites. *Geochim. Cosmochim. Acta* **74**, 1122–1145.
- Qin L., Xia J., Carlson R. W. and Zhang Q. (2015) Chromium stable isotope composition of meteorites. *46th Lunar Planet. Sci. Conf.*
- Reufer A., Meier M. M. M., Benz W. and Wieler R. (2012) A hit-and-run giant impact scenario. *Icarus* **221**, 296–299.
- Rhodes J. M. and Blanchard D. P. (1980) Chemistry of Apollo 11 low-K basalts. *11th Lunar Planet Sci. Conf.*, 49–66.
- Rhodes J. M., Hubbard N. J., Wiesmann H., Rodgers K. V., Brannon J. C. and Bansal B. M. (1976) Chemistry, classification and petrogenesis of Apollo 17 mare basalts. *Proc. Lunar Sci. Conf.* **7**, 1467–1489.
- Rhodes J. M., Blanchard D. P., Dungan M. A., Brannon J. C. and Rodgers K. V. (1977) Chemistry of Apollo 12 mare basalts: magma types and fractionation processes. *Proc. Lunar Sci. Conf.* **8**, 1305–1338.
- Roeder P. L. and Emslie R. F. (1970) Olivine-liquid equilibrium. *Contrib. Mineral. Petrol.* **29**, 275–289.
- Roeder P. L. and Reynolds I. (1991) Crystallization of chromite and chromium solubility in basaltic melts. *J. Petrol.* **32**, 909–934.
- Schauble, E., 2004. Applying stable isotope fractionation theory to new systems. In (eds. C. M. Johnson, B. Beard, F. Albarède), *Reviews in Mineralogy & Geochemistry*, 56, *Geochemistry of Non-traditional Stable Isotopes*. Mineralogical Society of America.
- Schediwiy S., Rosman K. J. R. and de Laeter J. R. (2006) Isotope fractionation of cadmium in lunar material. *Earth Planet. Sci. Lett.* **243**, 326–335.
- Schiller M., Van Kooten E., Holst J. C., Olsen M. B. and Bizzarro M. (2014) Precise measurement of chromium isotopes by MC-ICPMS. *J. Anal. At. Spectrom.* **29**, 1406–1416.
- Schoenberg R., Zink S., Staubwasser M. and von Blanckenburg F. (2008) The stable Cr isotope inventory of solid Earth reservoirs determined by double spike MC-ICP-MS. *Chem. Geol.* **249**, 294–306.
- Schoenberg R., Merdian A. A., Hassler K., Koch H., Holmden C., Kleinhanns I. C. and Wile M. (2015) No evidence for stable Cr isotope fractionation during planetary differentiation. *Gold-schmidt Abstract* **2015**, 2812.
- Schreiber H. D., Haskin L. A. (1976) Chromium in basalts: experimental determination of redox states and partitioning among synthetic silicate phases. *Proceedings of the 7th Lunar Science Conference*. Pergamon Press Inc, New York, pp. 1221–1259.
- Seifert S. and Ringwood A. E. (1988) The lunar geochemistry of chromium and vanadium. *Earth Moon Planet.* **40**, 45–70.
- Sharp Z. D., Shearer C. K., McKeegan K. D., Barnes J. D. and Wang Y. Q. (2010) The chlorine isotope composition of the Moon and implications for an anhydrous mantle. *Science* **329**, 1050–1053.
- Snyder G. A., Taylor L. A. and Neal C. R. (1992) A chemical model for generating the sources of Mare basalts: combined equilibrium and fractional crystallization of the lunar magma-sphere. *Geochim. Cosmochim. Acta* **56**, 3809–3823.
- Snyder G. A., Neal C. R., Taylor L. A. and Halliday A. N. (1997) Anatexis of lunar cumulate mantle in time and space: Clues from trace-element, strontium, and neodymium isotopic chemistry of parental Apollo 12 basalts. *Geochim. Cosmochim. Acta* **61**, 2731–2747.
- Spicuzza M. J., Day J. M. D., Taylor L. A. and Valley J. W. (2007) Oxygen isotope constraints on the origin and differentiation of the Moon. *Earth Planet. Sci. Lett.* **253**, 254–265.
- Taylor S. and Jakes P. (1974) The geochemical evolution of the Moon. *Proc. Lunar Sci. Conf.* **5**, 1287–1305.
- Touboul M., Kleine T., Bourdon B., Palme H. and Wieler R. (2009) Tungsten isotopes in ferroan anorthosites: implications for the age of the Moon and lifetime of its magma ocean. *Icarus* **199**, 245–249.
- Trinquier A., Birck J.-L. and Allègre C. J. (2007) Widespread Cr-54 heterogeneity in the inner Solar system. *Astrophys. J.* **655**, 1179–1185.
- Trinquier A., Birck J. L., Allègre C. J., Gopel C. and Ulfbeck D. (2008) ⁵³Mn-⁵³Cr systematics of the early Solar system revisited. *Geochim. Cosmochim. Acta* **72**, 5146–5163.
- Wadhwa M. (2008) Redox conditions on small bodies, the Moon and Mars. In (eds. G. J. MacPherson, D. W. Mittlefehldt, J. H. Jones, S. B. Simon). *Oxygen in the Solar System*, pp. 493–510.
- Warner R. D., Taylor G. J., Conrad G. H., Roy Northrop H., Barker S., Keil K., Ma M.-S. and Schmitt R. (1979) Apollo 17 hith-Ti mare basalts: New bulk compositional data, magma types and petrogenesis. *Proc. Lunar Sci. Conf.* **10**, 225–247.
- Warren P. H. (1985) The magma ocean concept and lunar evolution. *Ann. Rev. Earth. Planet. Sci.* **13**, 201–240.
- Warren P. H. and Taylor G. J. (2014) 2.9 – The Moon. In *Treatise on Geochemistry* (ed. H. D. H. K. Turekian), second ed. Elsevier, Oxford, pp. 213–250.
- Warren P. H. and Wasson J. T. (1979) Origin of KREEP. *Rev. Geophys.* **17**, 73–88.
- Weyer S., Anbar A. D., Brey G. P., Munker C., Mezger K. and Woodland A. B. (2005) Iron isotope fractionation during planetary differentiation. *Earth Planet. Sci. Lett.* **240**, 251–264.
- Wiechert U., Halliday A. N., Lee D. C., Snyder G. A., Taylor L. A. and Rumble D. (2001) Oxygen isotopes and the moon-forming giant impact. *Science* **294**, 345–348.
- Wieczorek M. A., Neumann G. A., Nimmo F., Kiefer W. S., Taylor G. J., Melosh H. J., Phillips R. J., Solomon S. C., Andrews-Hanna J. C., Asmar S. W., Konopliv A. S., Lemoine F. G., Smith D. E., Watkins M. M., Williams J. G. and Zuber M. T. (2013) The Crust of the Moon as Seen by GRAIL. *Science* **339**, 671–675.

- Willis J. P., Erlank A. J. and Gurney J. J., et al. (1972) Major, minor, and trace element data for some Apollo 11, 12, 14, and 15 samples. *3rd Lunar Sci. Conf.*, 1269–1273.
- Wood B. J., Bryndzia L. T. and Johnson K. E. (1990) Mantle oxidation state and its relationship to tectonic environment and fluid speciation. *Science* **248**, 337–345.
- Yin Q.-Z., Jacobsen B., Moynier F. and Hutcheon I. D. (2007) Toward consistent chronology in the early solar system: high-resolution Mn53-Cr53 chronometry for chondrules. *Astrophys. J.* **662**, 43–46.
- Zhang J., Dauphas N., Davis A. M., Leya I. and Fedkin A. (2012) The proto-Earth as a significant source of lunar material. *Nat. Geosci.* **5**, 251–255.

Associate editor: Qing-Zhu Yin