



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



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ABSTRACT

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

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1. Introduction

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

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

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

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

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

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

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

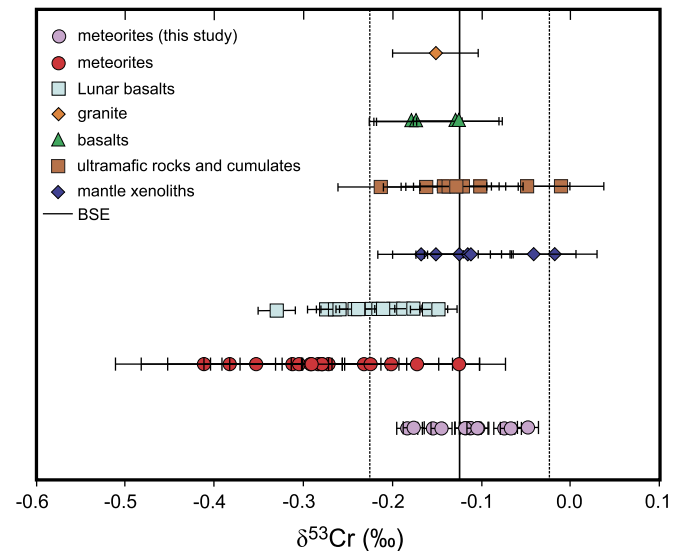


Fig. 1. Compilation of Cr data in high temperature rocks. The granite, basalts and ultramafic rocks and cumulates data are from Schoenberg et al. (2008), the meteorite data is from Moynier et al. (2011), Schiller et al. (2014) and this study. The lunar samples data is from Bonnand et al. (in press).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

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

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

2. Samples

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

3. Analytical methods

3.1. Metal–silicate experiments

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

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