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The nature of Earth's building blocks as revealed by calcium isotopes

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ABSTRACT

Calcium is the fifth most abundant element in the Earth and in chondrites and is a pure lithophile element which does not partition into planetary cores. Therefore, the calcium isotopic composition of the mantle represents the bulk Earth and calcium isotopes have the potential to reveal genetic links between Earth and meteorites. However, whether calcium exhibits significant mass-dependent variations among Earth and the various chondrite groups, and the magnitude of these variations, is still contentious. Here we have developed a new method to analyze calcium isotope ratios with high precision using multiple-collector inductively-coupled-plasma mass-spectrometry. The method has been applied to a range of terrestrial and meteoritic samples. We find that the Earth, the Moon, and the aubrite parent body are indistinguishable from enstatite, ordinary, and CO chondritic meteorites. Therefore, enstatite chondrites cannot be excluded as components of Earth's building blocks based on calcium isotopes, as has been proposed previously. In contrast, CI, CV, CM and CR carbonaceous chondrites are largely enriched in lighter calcium isotopes compared to Earth, and, overall, exhibit a wide range in calcium isotopic composition. Calcium is the only major element, along with oxygen, for which isotopic variations are observed among carbonaceous chondrite groups. These calcium isotope variations cannot be attributed to volatility effects, and it is difficult to ascribe them to the abundance of isotopically light refractory inclusions. The calcium isotope data presented in this study suggest that both ordinary and enstatite chondrites are representative of the bulk of the refractory materials that formed Earth. On the basis of calcium isotopes, carbonaceous chondrites (with the exception of CO) are not representative of the fraction of condensable material that accreted to form the terrestrial planets and can be excluded as unique contenders for the building blocks of Earth; however, on the basis of other isotopic systems, CO chondrites can be excluded as well.

1. Introduction

Isotopic ratios have traditionally been used as tracers of the genetic link between meteorites and the Earth (e.g. Clayton, 2003; Trinquier et al., 2007; Warren, 2011). Mass-dependent isotopic differences between and within planetary bodies and meteorites are records of the prevailing conditions (i.e. initial heterogeneities) during their formation and the processes that altered them (e.g. condensation and accretion) during the early history of the solar system (e.g. Davis and Richter, 2007, 2014; Simon and DePaolo, 2010). These differences may also be ascribed to post-accretional, phase separation processes such as core formation (e.g. Georg et al., 2007; Moynier et al., 2011; Savage and Moynier, 2013) and/or large-scale evaporation (e.g. Paniello et al., 2012). Therefore, an understanding of the subtle isotopic differences between Earth and meteorite groups can help elucidate the processes by which terrestrial planets were assembled and identify the type(s) of extant meteorites that are representative of precursor material that accreted into the proto-Earth (Javoy, 1995; Javoy et al., 2010; Simon and DePaolo, 2010; Huang et al., 2012).

Particularly useful materials for study are primitive meteorites (chondrites), which escaped the planetary differentiation process. With the exception of the most volatile elements, type CI chondrite elemental abundances match solar photospheric abundances (and therefore, solar system abundances, given that the sun represents over 99.86% of the solar system's mass; Anders and Grevesse, 1989; Lodders, 2003). Taken in conjunction, these facts give credence to the historical use of chondrites to constrain the refractory lithophile (RLE) element composition of bulk silicate Earth (BSE) and other planets (e.g. Allègre et al., 1995; McDonough and Sun, 1995).

Of the major chondritic meteorite groups, the enstatite (E-) chondrites, though most remote from BSE estimates in terms of

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elemental concentrations (e.g. calcium, aluminum, iron, and zinc; Javoy, 1995) and oxidation state (Mason, 1966; Keil, 1989), are the most similar to Earth with regard to high temperature mineral composition, and importantly, the isotopic composition of most major and minor elements studied thus far, including nickel (Regelous et al., 2008), nitrogen (Javoy et al., 1986), chromium (Birck et al., 1999; Trinquier et al., 2007), and strontium (Moynier et al., 2012). This is true of oxygen also, for which the isotopic composition of E-chondrites is identical to that of Earth despite varying significantly among different chondrite groups (Clayton et al., 1984). The isotopic similarities between E-chondrites and Earth do not, in most cases, hold true for the ordinary (O-) and carbonaceous (C-) chondrite groups, which has led some authors to propose E-chondrites as Earth's primary accretional material (Javoy, 1995; Javoy et al., 2010). Exceptions to the similarity between E-chondrites and Earth are titanium (recently observed to fractionate mass-independently between the two; Zhang et al., 2012b), silicon (which exhibits more significant, mass dependent variations; e.g. Fitoussi and Bourdon, 2012, and Savage and Moynier, 2013), and possibly calcium (e.g. Simon and DePaolo, 2010). These exceptions pose challenges to the E-chondrite model of Earth. The difference in silicon isotopic composition between Earth and E-chondrites cannot easily be attributed to metal/silicate fractionations during planetary core formation because an unrealistically large amount of silicon would need to be placed in the core to satisfy mass balance equations (Fitoussi and Bourdon, 2012; Savage and Moynier, 2013). Nonetheless, silicon's sensitivity to post-accretional processes makes its use as an accretional tracer difficult.

On the other hand, calcium is an ideal tracer of planetary accretion processes because it is sensitive to the mechanisms involved in planet formation but is little affected by subsequent processing: as a RLE, calcium does not fractionate with respect to other RLE during its high-temperature condensation and does not volatilize or sink into the core during accretion and differentiation of a planet (Rubin, 2011). Therefore, it provides a good record of early solar system conditions. Mass-dependent isotopic variations of calcium between chondrite groups and Earth have not been as intensely studied but can provide important information for identifying the building blocks of Earth (DePaolo, 2004).

Calcium is the fifth most abundant lithophile element in the rocky planets. It has a relatively large mass difference between isotopes and therefore, mass-dependent fractionations are amplified. The element is composed of five stable isotopes: ^{40}Ca (96.94%), ^{42}Ca (0.647%), ^{43}Ca (0.135%), ^{44}Ca (2.086%), ^{46}Ca (0.004%), and one radioactive isotope that is treated as a stable isotope because of its very long half-life: ^{48}Ca (4.3×10^{19} years; 0.187%).

Recent studies have documented mass-dependent variations of calcium between the major chondrite groups and Earth, but the character and magnitude of these variations are still debated. Whether the calcium isotopic composition of the BSE is the same as that of E-chondrites is particularly contentious. Simon and DePaolo (2010) found that E-chondrites exhibit distinct enrichments of up to 0.4‰ in the heavier isotopes of calcium relative to Earth. Carbonaceous chondrites, though, were found to be enriched in the lighter isotopes of calcium. Ordinary chondrites, lunar and martian basalts, angrites, diogenites, and eucrites were measured to be isotopically identical to Earth. These results suggest that calcium in O-chondrites is representative of the bulk of the calcium that formed the terrestrial planets and that calcium in E- and C-chondrites is not. This is at odds with evidence from the other isotopic systems mentioned above. Another surprising result was that E-chondrites and E-achondrites (aubrites, which are identical to E-chondrites with regard to other isotopic systems, e.g. Clayton and Mayeda, 1996), show dissimilar calcium isotopic compositions according to Simon and DePaolo. In contrast to Simon and DePaolo (2010), Huang and Jacobsen (2012), find both E-chondrites and O-chondrites to be identical to Earth in terms of Ca isotopes. A consistency between the two studies, however, is that CV and CM chondrites were observed to be enriched in light calcium isotopes compared to Earth.

In order to compare the calcium isotopic composition of chondrites with the BSE it is critical to establish a stable terrestrial mantle value. Previous terrestrial calcium isotopic studies have focused primarily on modern and ancient marine carbonates and sulphates (e.g. Fantle and Tipper, 2014); yet, detailed work on igneous rocks is fairly limited (Skulan et al., 1997; Amini et al., 2009; Huang et al., 2009, 2010). Variations of 0.3‰ in the ^{44}Ca/^{40}Ca of Makapuu-stage Koolau lavas were reported by Huang et al. (2011); these were interpreted as a result of recycling ancient carbonate into the mantle. Within the mantle, Huang et al. (2010) found that calcium in peridotite orthopyroxenes is isotopically heavier than in clinopyroxenes and that basalts are therefore isotopically fractionated compared to their source rocks. Mass balance calculations using the abundances of different calcium-bearing minerals in basalts and their isotopic compositions yielded a $\delta^{44}\mathrm{Ca}_{\mathrm{SRM\,915a}}$ value (permil deviation of the ^{44}Ca/^{40}Ca ratio from the standard SRM 915a) for the BSE of 1.05 ± 0.05‰. This represents the current best estimate of the BSE composition; however, Huang et al. (2010) admit that this value is based on a very limited sample set and that more terrestrial samples need to be analyzed in order to better constrain the BSE composition.

In this study we present calcium isotopic measurements of terrestrial and extraterrestrial material made by multiple-collector inductively-coupled-plasma mass-spectrometry (MC-ICP-MS) using the sample-standard bracketing technique. Our method differs from that which is used by Huang et al. (2010, 2011), Huang and Jacobsen (2012) and Simon and DePaolo (2010), whose calcium studies utilize isotopic double spike combined with Thermo-Ionization Mass-Spectrometry (TIMS). The goal of our study is to resolve the isotopic compositions of chondritic groups and to compare them to a confident value for BSE in order to reveal the nature of Earth's building blocks. We therefore present high-precision calcium isotopic data for an extensive set of meteoritic samples (including C-chondrites of most sub-types, O-chondrites, E-chondrites, and aubrites) and several Apollo-collected lunar basalts and glasses. For the purpose of comparison, we report a comprehensive data set for ocean island basalts (OIB). Samples were chosen to represent a range of mantle end-members and intermediaries in order to test the calcium homogeneity of the Earth's mantle and also to test the accuracy of our method against double-spike TIMS.

2. Samples and analytical procedures

2.1. Samples

A range of terrestrial and meteoritic samples was analyzed, including five E-chondrites, 10 C-chondrites representing most subgroups (CI, CV, CO, CM, CR), three O-chondrites, five lunar basalts and glasses, and two terrestrial rock standards. In addition, we measured OIB from a series of compositional ranges (DMM, HIMU, EM1, and intermediaries) to estimate the calcium isotopic composition of the mantle. We also analyzed five aubrites (E-achondrites of igneous origin) and performed leaching experiments on one E-chondrite in order to evaluate the isotopic composition of the mineral oldhamite (CaS), a significant carrier of calcium in meteorites. Since oldhamite is water soluble and calcium very easily aqueously mobilized, a possible origin for the difference in E-chondrite results among studies lay in heterogeneous distribution of oldhamite in dissolved samples.