Calcium-48 isotopic anomalies in bulk chondrites and achondrites: Evidence for a uniform isotopic reservoir in the inner protoplanetary disk

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ABSTRACT

Thermal ionization mass spectrometry (TIMS) was used to measure the calcium isotopic compositions of carbonaceous, ordinary, enstatite chondrites as well as eucrites and aubrites. We find that after correction for mass-fractionation by internal normalization to a fixed $^{42}Ca/^{44}Ca$ ratio, the $^{43}Ca/^{44}Ca$ and $^{46}Ca/^{44}Ca$ ratios are indistinguishable from terrestrial ratios. In contrast, the $^{48}Ca/^{44}Ca$ ratios show significant departure from the terrestrial composition (from -2 ε in eucrites to $+4$ ε in CO and CV chondrites). Isotopic anomalies in $\varepsilon^{48}Ca$ correlate with $\varepsilon^{50}Ti$: $\varepsilon^{48}Ca = (1.09 \pm 0.11) \times \varepsilon^{50}Ti + (0.03 \pm 0.14)$. Further work is needed to identify the carrier phase of ^{48}Ca–^{50}Ti anomalies but we suggest that it could be perovskite and that the stellar site where these anomalies were created was also responsible for the nucleosynthesis of the bulk of the solar system inventory of these nuclides. The Earth has identical ^{48}Ca isotopic composition to enstatite chondrites (EH and EL) and aubrites. This adds to a long list of elements that display nucleosynthetic anomalies at a bulk planetary scale but show identical or very similar isotopic compositions between enstatite chondrites, aubrites, and Earth. This suggests that the inner protoplanetary disk was characterized by a uniform isotopic composition (IDUR for Inner Disk Uniform Reservoir), sampled by enstatite chondrites and aubrites, from which the Earth drew most of its constituents. The terrestrial isotopic composition for ^{17}O, ^{48}Ca, ^{50}Ti, ^{62}Ni, and ^{92}Mo is well reproduced by a mixture of 91% enstatite, 7% ordinary, and 2% carbonaceous chondrites. The Earth was not simply made of enstatite chondrites but it formed from the same original material that was later modified by nebular and disk processes. The Moon-forming impactor probably came from the same region as the other embryos that made the Earth, explaining the strong isotopic similarity between lunar and terrestrial rocks.

1. Introduction

The discovery of departures from the laws of mass-dependent fractionation for oxygen isotopes in meteorites and planets showed that the solar nebula was never fully homogenized (Clayton et al., 1973). The origin of these anomalies is still debated and may have involved gas phase chemistry (Clayton, 2002; Yurimoto and Kuramoto, 2004; Lyons and Young, 2005; Chakraborty et al., 2013).

Isotopic anomalies of clear nucleosynthetic origin were found for various elements such as calcium and titanium in refractory inclusions (Lee et al., 1978; Niederer et al., 1980; Niemeyer and Lugmair, 1981), hibonite-rich grains (Fahey et al., 1987a; Ireland, 1990), and presolar grains in meteorites (Ireland et al., 1991; Amari et al., 1992; Hoppe et al., 1994, 1996; Nittler et al., 1996). The finding of molybdenum isotopic anomalies in iron meteorites, which come from asteroids up to ~300 km in size, showed that some of these nucleosynthetic anomalies left their imprints on bulk planetary bodies (Dauphas et al., 2002c, 2004; Burkhardt et al., 2011). Most elements affected by isotopic anomalies are present in planetary materials at trace to minor element levels.

Calcium is a major lithophile refractory element that is ubiquitous in terrestrial rocks and meteorites. Previous studies have revealed the presence of isotopic anomalies of nucleosynthetic origin for calcium in presolar grains (Amari et al., 1992; Hoppe et al., 1996; Nittler et al., 1996), calcium–aluminum-rich inclusions—CAIs (Lee et al., 1978, 1979; Niederer and Papanastassiou, 1984; Papanastassiou and Brigham, 1989; Chen et al., 2010; Moynier et al., 2010), hibonite-rich grains (Zinner et al., 1986; Fahey et al., 1987a; Ireland, 1990), and acid leachates of primitive chondrites (Moynier et al., 2010). Simon et al. (2009) reported hints for the presence of small ^{40}Ca isotope anomalies in bulk chondrites and H.-W. Chen et al. (2011) found evidence for ^{48}Ca isotope anomalies in several groups of achondrites. Here, we report calcium isotope measurements of various groups of meteorites that have never been analyzed before.

Identifying isotope anomalies for the neutron-rich isotope ^{48}Ca is important because it is the isotope that can be most unambiguously tied to type Ia supernovae (SNIa, Meyer et al., 1996; Woosley, 1997). Several studies have reported the presence of neutron-rich isotopic anomalies at the scale of bulk planetary objects for iron-peak elements, such as ^{48}Ca (H.-W. Chen et al., 2011), ^{50}Ti (Niederer et al., 1985b; Niemeyer, 1985, 1988; Trinquier et al., 2009; Zhang et al., 2011, 2012), ^{54}Cr (Shukolyukov and Lugmair, 2006; Trinquier et al., 2007; Qin et al., 2010), and ^{64}Ni (Steele et al., 2011; Tang and Dauphas, 2014). The carrier of ^{54}Cr isotope anomalies has been identified by NanoSIMS as ^{54}Cr-rich nano-oxide/nanospinel grains of supernova origin (Dauphas et al., 2010; Qin et al., 2011). It is uncertain at the present time whether these grains were derived from core collapse (ccSN) or type Ia (SNIa) supernovae. Despite the fact that SNIa are thought to contribute approximately half of the total iron in the solar system (Heger et al., 2014), no presolar grains of unambiguous SNIa origin have been found so far in meteorites and no dust has been detected by spectroscopy in the aftermath of SNIa explosions. Unlike ccSN, where most of the explosion energy goes into blowing off the massive hydrogen envelope, the ejecta from SNIa is accelerated to high velocities. The gas density in SNIa ejecta is more than three orders of magnitude lower than in ccSN ejecta, so the grains that condense (*e.g.*, Fe, Ni, Si, FeS, SiO_2, Mg_2SiO_4, $MgSiO_3$, Al_2O_3, C) should be smaller than a few tens of nm (Nozawa et al., 2011). A significant fraction of these grains should be destroyed by shocks during their injection in the interstellar medium (ISM). Some of the matter ejected from SNIa could also condense as coatings on preexisting ISM grains. Although SNIa are not efficient at producing dust, further work is needed to tell whether the presolar carriers of neutron-rich isotope anomalies in meteorites are of SNIa or ccSN origin.

In an effort to understand what controls the presence of isotopic anomalies in the solar system, we have measured all calcium isotopes except ^{40}Ca by thermal ionization mass spectrometry (TIMS) in many meteorites that we had analyzed previously for ^{50}Ti and have discovered widespread ^{48}Ca isotope anomalies.

2. Analytical methods

2.1. Chemical separation

To facilitate comparison, the calcium isotope measurements were done on the same solutions that were analyzed previously for titanium (Zhang et al., 2011, 2012) and the reader is referred to these publications for details on the digestion method and the titanium–calcium separation step. The bulk meteorite samples weighing 100–150 mg were digested at ∼180 °C in high-pressure Parr bombs. After digestion, the solutions were dried down and the samples were taken up in 5 mL of 12 M HNO_3 + 0.2 M H_3BO_3. These solutions were loaded on a 2 mL Eichrom TODGA

cartridges and calcium was collected with other elements in 10 mL of 12 M HNO_3 while titanium remained on the columns. Titanium was further purified and analyzed at the University of Chicago on a ThermoFinnigan Neptune mass spectrometer upgraded with a Jet pump (Pfeiffer OnTool Booster) and jet cones.

The cuts containing most of the calcium were further purified at the Jet Propulsion Laboratory. Approximately 1 mg of Ca was separated by conventional cation ion exchange column chemistry (Bio-Rad AG 50W-X8 resin, 2 mL) in hydrochloric acid (Tera et al., 1970; Russell et al., 1978). This method provided excellent potassium–calcium separation as $^{40}K^+/^{40}Ca^+$ ratios were typically less than 10^{-7} during analyses and never required significant interference corrections. Efficient separation of magnesium and iron was also achieved. To eliminate aluminum, a small TODGA resin column (0.1 mL) was used. In dilute nitric acid, calcium is strongly adsorbed by the TODGA resin while aluminum and magnesium are not retained (Pourmand and Dauphas, 2010). The calcium cut from the first column was evaporated to dryness and dissolved in a few drops of concentrated HNO_3. The sample was dried down, re-dissolved in 0.1 mL 1 M HNO_3 and loaded onto the TODGA column. The resin was rinsed twice with 0.3 mL 1 M HNO_3 to remove aluminum and magnesium. After calcium was collected in 0.5 mL 0.25 M HCl and evaporated to dryness, the sample was oxidized with a few drops of concentrated HNO_3 and re-dissolved in 0.1 mL 7 M HNO_3. The calcium sample was loaded onto a column containing 0.1 mL Eichrom TRU spec resin. The resin was rinsed with 0.3 mL 7 M HNO_3 and calcium was collected in the load and rinse solutions. This step removes any residual titanium (in order to eliminate potential interferences of titanium on ^{46,48}Ca) and iron. The total chemistry yield was >85% for calcium and the procedural blank was negligible (∼30 ng). Samples were loaded on zone-refined rhenium filaments previously outgassed at 4.5 A (∼1800 °C) for 60 min. Double filaments were used for the analyses. Aliquots of 1–2 μg Ca were evaporated prior to loading onto the filaments and were then re-dissolved in one drop of 0.5 N H_3PO_4. Samples and standards were then loaded on the filaments as calcium phosphate (Caro et al., 2010).

2.2. Mass spectrometry

The very large dynamic range between the most and least abundant calcium isotopes ($^{40}Ca/^{46}Ca \approx 2.4 \times 10^4$) presents a formidable challenge to precise isotopic analysis by mass spectrometers (the abundances of calcium isotopes are ^{40}Ca: 96.941%, ^{42}Ca: 0.647%, ^{43}Ca: 0.135%, ^{44}Ca: 2.086%, ^{46}Ca: 0.004%, ^{48}Ca: 0.187%). Because of the 20% mass difference for calcium isotopes and the potential for radiogenic effects in ^{40}Ca, we did not measure the high intensity ^{40}Ca ion beam and only analyzed isotopes ^{42}Ca to ^{48}Ca. All measurements were made with a multicollector ThermoFinnigan Triton at the Jet Propulsion Laboratory using 1) a *multidynamic mode*, where the magnetic field was switched during analysis to measure either ^{44}Ca or ^{46}Ca in the central collector (configuration 1: ^{42,43,44,46}Ca and configuration 2: ^{43,44,46,48}Ca), and 2) a *static mode*, where the magnetic field stayed fixed (configuration 3: ^{42,43,44,46,48}Ca). The analytical parameters for both modes are summarized in Table 1. Multicollector instruments have a relatively open structure and can be subject to the effects of secondary electrons. Using the multidynamic mode and assigning ^{44}Ca to the center cup (configuration 1) we observed, from time to time, when ^{40}Ca exceeded ∼0.3 nA (*i.e.*, 30 V on a 10^{11} Ohm resistor), small negative depressions (∼0.15 mV or ∼1.5×10^{-15} A) on the baselines, in particular around ^{46}Ca, resulting in a lower (and erroneous) $^{46}Ca/^{44}Ca$ ratio as compared to that measured by assigning ^{46}Ca to the center cup (configuration 2). We postulated that the negative depressions of the baselines were from secondary electrons produced by interaction of $^{40}Ca^+$ ions (0.35–0.45 nA) with