

CALCIUM ISOTOPE COMPOSITION OF METEORITES, EARTH, AND MARS

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ABSTRACT

The relative abundances of calcium isotopes in the mass range 40–44 were measured in primitive and differentiated meteorites and igneous rocks from Earth and Mars in search of non-mass-dependent variations that could provide clues about early solar system processes. Most bulk samples of planetary materials have calcium isotopic compositions identical with Earth's within the current resolution of about 0.01% in $^{40}\text{Ca}/^{44}\text{Ca}$. Possible exceptions include carbonaceous chondrites, some ordinary chondrites, and two samples of calcium–aluminum-rich inclusions, which have small excesses of ^{40}Ca . The samples with ^{40}Ca excesses are also known to have ^{50}Ti and ^{135}Ba excesses and ^{142}Nd and ^{144}Sm deficits. Collectively these data from refractory elements suggest that the planetary embryos represented by chondrites preserve isotopic heterogeneity that reflects different nucleosynthetic sources. No late admixture from a single nucleosynthetic source can explain all observations. The results are most compatible with variable proportions of material derived from Type II supernovae. The initial calcium isotope compositions of Earth and Mars are indistinguishable and similar to the ^{40}Ca abundance found in some chondrites and all differentiated meteorites studied. It appears that isotopic heterogeneity in calcium was still present at the completion of disk formation but was homogenized during planetary accretion.

Key words: minor planets, asteroids – planetary systems: protoplanetary disks – solar system: formation – stars: AGB and post-AGB – supernovae: general

1. INTRODUCTION

The synthesis of calcium isotopes in stars is complex and the isotopes are generally produced in proportions that are quite different from the average terrestrial or solar proportions (e.g., Busso et al. 2003; Rauscher et al. 2002). This suggests that calcium in the solar system reflects a mixture of stellar source components. The detailed record of isotopic heterogeneity preserved in meteorites can help to identify what types of stars were present in the local star-forming region at the time the solar system started to form, and in some instances clarify the characteristics of the stellar interiors and explosions involved.

Over 30 years of study have resulted in evidence for substantial isotopic heterogeneity among early-formed solid objects in the solar system. Isotopic differences between meteorite parent bodies, Earth, and Mars due to non-mass-dependent processes are well known for oxygen isotopes (Clayton & Mayeda 1983) but not for the other major chemical constituents of rocky planets (Fe, Si, Mg, Ca). The origin of the oxygen isotope variations is uncertain, partly because oxygen was present in solids, fluids, and gas in the solar nebula and consequently could have been modified by processes *within* the nebula that would not have affected the other more refractory elements (e.g., Clayton 2002; Lyons & Young 2005). The question that remains is whether there was heterogeneity within the solar nebula that was inherited from different presolar nucleosynthetic sources, and preserved long enough to be recorded in small planetary bodies. Isotope anomalies in bulk primitive meteorites (chondrites) have been reported for titanium (Leya et al. 2008; Niederer et al. 1985; Niemeyer 1988), chromium (Podosek et al. 1997; Rotaru et al. 1992; Shukolyukov & Lugmair 1993; Trinquier et al. 2008), zirconium (Sanloup et al. 2000; Schönbachler et al. 2005), molybdenum (Chen et al. 2004; Dauphas et al. 2002a, 2002b; Yin & Jacobsen 2000; Yin et al. 2002a), ruthenium (Chen et al. 2003; Papanastassiou et al. 2004), barium (Carlson et al. 2007; Hidaka et al. 2003; Ranen &

Jacobsen 2006), neodymium (Carlson et al. 2007), samarium (Andreasen & Sharma 2006), osmium (Brandon et al. 2005), and tungsten (Qin et al. 2008). For some elements, in particular barium, neodymium, and samarium, the extent of the effects is still the subject of some debate. For molybdenum, ruthenium, and osmium the effects have not been confirmed by subsequent studies (e.g., Becker & Walker 2003; Lee & Halliday 2002; Yokoyama et al. 2007). For these reasons, except for the effects in oxygen and possibly titanium and chromium, evidence that the initial heterogeneity was not entirely erased by mixing within the nebula before planets started to form remains controversial. It is clear from samples of presolar grains, as well as from samples of early-formed solid objects (i.e., the refractory calcium–aluminum-rich inclusions (CAIs) and chondrules), that there were several isotopically distinct components incorporated into the nebula. For example, large isotopic variations in calcium isotopes have been found in CAIs; the best-documented calcium isotope effects are excesses of ^{48}Ca and depletions of ^{46}Ca (Ireland et al. 1991; Jungck et al. 1984; Lee et al. 1979; Niederer & Papanastassiou 1984; Russell et al. 1978, Russell et al. 1998;).

The reported differences in the isotopic abundances of refractory elements such as barium (Andreasen et al. 2008; Carlson et al. 2007; Ranen & Jacobsen 2006), neodymium, and samarium (Andreasen & Sharma 2006; Boyet & Carlson 2005; Carlson et al. 2007) between bulk meteorites and the Earth, suggest that heterogeneity in the solar nebula was preserved through part of the accretion process. These recent observations support earlier barium isotope measurements of chondrite leaches by Hidaka et al. (2003) and contrast to some degree with predictions based on dynamical models that mixing and homogenization of the nebula was highly efficient (cf. Boss 2004). The observations of heterogeneity are important because the subtle differences may be useful for reconstructing the processes by which planets were assembled (e.g., Weidenschilling 2000), and for deducing from where within the nebula the materials came (Lugmair & MacIsaac 1995). The heterogeneity may have come

from generations of star formation that predated the molecular cloud that collapsed to form the solar system, and/or been carried over to the solar nebula because during triggered collapse the injected dust grains would only penetrate the outer layers of the presolar cloud (Margolis 1979). Materials injected late into the collapsing cloud (Foster & Boss 1997) might also be the last to fall onto the collapsing protostellar disk, and hence might provide both a temporal and spatial signal that could be useful for discerning the relationships between planetesimal formation, radial transport within the disk, and infall onto the plane of the disk. Since the discovery of the first oxygen isotopic anomalies in meteorites some 35 years ago (Clayton et al. 1973a), there has been growing awareness of the connections between geology, meteorite studies, cosmochemistry, and astrophysics.

2. CALCIUM ISOTOPE MEASUREMENTS

This study reports calcium isotopic compositions for thirteen igneous rocks from Earth, eight achondrites (including four Martian meteorites), nine primitive chondritic meteorites, and two igneous refractory inclusions from chondritic meteorites. The achondrites, which have similarities to igneous rocks from Earth, come from differentiated parent bodies (i.e., they have been melted, homogenized, and yield igneous textures). The chondrites are undifferentiated and reflect heterogeneous mixtures of early solar system materials (components such as the refractory inclusions) that have not been processed at the high temperatures and pressures of planetary interiors.

All measurements reported here were obtained on unspiked samples using thermal ionization mass spectrometry (TIMS). A majority of the powdered samples were dissolved in a mixture of hydrofluoric and perchloric acids (HF-HClO₄), followed by nitric acid (HNO₃), and centrifuged. A few samples were dissolved under higher pressure in Parr bombs without HClO₄. In most cases centrifuged residua have negligible mass. It is improbable that any undissolved refractory materials (e.g., presolar diamond, SiC, Al₂O₃, and rare MgAl₂O₄ and Si₃N₄) would contain a significant amount of calcium. Calcium was purified on standard cation exchange columns (Marshall & DePaolo 1989; Russell et al. 1978), except for carbonaceous chondrites Murray and Vigarano and one refractory inclusion in which it was separated on a combination of Eichron DGA/Sr spec resin at Washington University in St. Louis. At the Center for Isotope Geochemistry, University of California at Berkeley it was found that a second pass through the cation exchange resin (AG-50W-X8) reduced aluminum, allowing for greater beam stability and intensity in samples with high Al/Ca ratios. For consistency, the second column pass was used for all samples.

A ⁴³Ca spike was used to determine column blanks and yields. The combined blank and yield for two column passes were ~14 ng (<0.5% of the sample loaded on each filament) and ~99.5%, respectively. Calcium isotope ratios were measured with a Thermo-Finnigan Triton TIMS instrument at the Center for Isotope Geochemistry, University of California, Berkeley (Table 1). The ⁴⁰Ca⁺, ⁴²Ca⁺, ⁴³Ca⁺, and ⁴⁴Ca⁺ ion beams were measured simultaneously in a static cup configuration, with the intensity of the ⁴⁰Ca⁺ beam adjusted to be in the range of (2–3) × 10⁻¹⁰ Å. Masses 46 and 48 were not measured for most analyses; the required multidynamic analysis, their low abundances, and mass interferences from titanium isotopes make them more difficult to measure accurately. The ion source of the Thermo-Finnigan Triton mass spectrometer uses a face-to-face double-filament configuration. The calcium samples are measured with

a filament temperature of 1400–1450 °C, a range that primarily reflects the temperature of the ionization filament but is slightly enhanced by the presence of the second, cooler sample filament. Calcium isotope ratio data were collected in 10 groups of 20 cycles each, over a period of about 120 minutes. The in-run analytical precision, calculated as two standard deviations of the mean of the 200 measured ratios, was typically 0.002% of the ⁴⁰Ca/⁴⁴Ca ratio. External (sample-to-sample) reproducibility is larger than 0.002% and is estimated to be ~0.007% after all sources of error are considered (further discussion below). Sample uncertainties are reported as two standard deviations of the mean or twice the standard error ($\sigma_{\text{mean}} = SD/\sqrt{n}$) based on *n* separate mass spectrometer runs. An exponential law was used for the instrumental mass discrimination correction using ⁴²Ca/⁴⁴Ca = 0.31221 for normalization (Marshall & DePaolo 1989; Russell et al. 1978). Variations in ⁴⁰Ca are reported as $\epsilon_{40/44} = \ln(^{40}\text{Ca}/^{44}\text{Ca}_{\text{measured}}/47.1487) \times 10^4$ that corresponds to the preferred ⁴⁰Ca/⁴²Ca value of 151.016 (Marshall & DePaolo 1989; Russell et al. 1978).

An intensive two-year analytical campaign (including >200 standard runs specifically for this work) revealed that Faraday cup collector efficiencies, especially for the cup used to measure the abundant isotope ⁴⁰Ca, can change and affect measured ⁴⁰Ca abundances. This effect, also reported elsewhere for similar instruments (e.g., Andreasen & Sharma 2006), is interpreted to reflect modification of the carbon lining of the collector due to accumulated plated calcium. The Faraday cup liners have a lifetime of a few to several months, depending on usage. When too much Ca has accumulated, the reproducibility of the standards degrades and there is a systematic shift toward lower ⁴⁰Ca/⁴⁴Ca ratios. When this effect is observed, the graphite liners in the compromised Faraday cups are replaced, the period of degradation of the cups is noted, and any sample data taken while the cups were compromised is discarded. After replacement of the liners, there is generally a small but significant shift in the measured ⁴⁰Ca/⁴⁴Ca ratios of the standards, but this new standard ratio then remains stable for months afterward. To account for these discrete offsets, our sample analyses are normalized to stable blocks of running average analyses of the BCR-1 basalt standard and/or the SRM915A carbonate standard, and the data used are only those collected when the standard values were unchanging.

Based on our analyses of the SRM915A standard over these stable times, the reproducibility of our measurements is ±0.61 ϵ -units (2 SD, *n* = 17) for $\epsilon_{40/44}$ and ±1.65 ϵ -units for $\epsilon_{43/44}$. The value of two standard errors of the mean ($2\sigma_{\text{mean}}$) for the groups of three standard analyses is also ±0.6 ϵ -units. The uncertainties on ⁴⁰Ca/⁴⁴Ca for our sample measurements, calculated from the results of 2–12 mass spectrometer runs normalized using the shifts in standard values where necessary, are in the range ±0.09 to ±1.33 ϵ -units, with an average value of ±0.75 ϵ -units. This latter value is similar to the reproducibility of the standards, and we consider this to be a good estimate of the reliability of the reported ⁴⁰Ca/⁴⁴Ca ratios; although the calculated $2\sigma_{\text{mean}}$ (here after notated as 2σ) values vary, these variations are probably not as significant as the average value of ±0.75. Between the time at which this contribution was submitted and the Editor's request to alleviate concerns of a reviewer, the Faraday cup liners were replaced again. As a consequence, measurements of the chondrites Murray and Vigarano and the refractory inclusions, along with additional replicate measurements (in total 24 sample measurements), were made using a fresh set of cup liners. These recent measurements were made using an improved cup

configuration in which ^{46}Ca and ^{48}Ca beams were included in the analysis. The reproducibility throughout the entire study (2007 June–2008 October), including the added uncertainty related to our use of several sets of cup liners, based on the SRM915A standard was $\pm 0.89 \epsilon$ -units (2 SD, $n = 27$) for $\epsilon_{40/44}$ and $\pm 1.50 \epsilon$ -units for $\epsilon_{43/44}$.

To demonstrate the precision with which we can resolve differences in $\epsilon_{40/44}$ we prepared and analyzed mixtures of the SRM915A standard with ^{40}Ca -enriched calcium separated from a 1.26 Ga sample of granophyre from the Muskox Intrusion (cf. Stewart & DePaolo 1992), sample DM-40 ($\epsilon_{40/44} = 29.3$), to produce reference materials with slightly higher than normal $\epsilon_{40/44}$ values (~ 2.5 and 4.5ϵ -units; determined gravimetrically, see Table 1). A comparison between the gravimetric and mass spectrometry results indicates that we match $\epsilon_{40/44}$ values to $\leq 0.85 \epsilon$ -units (or 85 ppm; see Figure 1), and can resolve $\leq 0.5 \epsilon$ -units (≤ 50 ppm) relative differences in $\epsilon_{40/44}$. We reanalyzed samples measured by Marshall & DePaolo (1989) as a further check on our results. Their average $^{40}\text{Ca}/^{42}\text{Ca}$ ratio of four terrestrial basaltic lavas is $151.024 \pm 14 (2\sigma)$, which compares favorably to our average basalt value of $151.018 \pm 2 (2\sigma, n = 5$ excluding continental basalt BCR-1) measured on a slightly different subset of basalts, a different mass spectrometer, and with simultaneous multicollection rather than sequential, time-corrected measurements with a single-collector mass spectrometer.

Thirty-three replicate measurements of four achondrites and five oceanic basalts are used to define the initial terrestrial calcium isotopic composition (see Figure 1). The weighted means of the nine samples, $^{40}\text{Ca}/^{44}\text{Ca} = 47.1480 \pm 4 (2\sigma)$ and $^{43}\text{Ca}/^{44}\text{Ca} = 0.064868 \pm 1 (2\sigma)$ are consistent with previous determinations by Russell et al. (1978) and Marshall & DePaolo (1989) and equivalent to a $^{40}\text{Ca}/^{42}\text{Ca}$ value of $151.0150 \pm 13 (2\sigma)$. Changes in the abundance of ^{40}Ca relative to other calcium isotopes can originate from nucleosynthesis in stars, but also from the radioactive decay of ^{40}K to ^{40}Ca by electron (β^-) emission (half-life of 1.27 billion years). The mantles of both Earth and Mars have small amounts of ^{40}K in comparison to ^{40}Ca (present value of $^{40}\text{K}/^{40}\text{Ca} \approx 10^{-6}$) and therefore radioactive decay over the 4.57 billion year history of the solar system produces a ≤ 0.1 to 0.2ϵ -unit increase in $\epsilon_{40/44}$. Due to higher K/Ca ratios in some chondrites, radioactive decay can produce up to $\sim 1.1 \epsilon$ -unit increase in ^{40}Ca over the age of the solar system. Both measured and decay-corrected values for $\epsilon_{40/44}$ are given in Table 1.

Most measured oceanic basalts and silicic igneous rocks from Earth yield initial $\epsilon_{40/44}$ values indistinguishable from zero (Figure 1), which indicates that the $^{40}\text{Ca}/^{44}\text{Ca}$ ratio of the Earth's mantle (and hence the bulk Earth) is well defined and virtually invariant at the resolution of our measurements. Samples DM-40 and DM-10 from the evolved marginal member of the Precambrian Muskox layered igneous intrusion yield large measured ^{40}Ca excesses of $29.32 \pm 1.96 (2\sigma)$ and $3.24 \pm 0.24 (2\sigma)$, respectively. An early Eocene two-mica granite from southern Arizona also shows a resolvable ^{40}Ca excess of $1.12 \pm 0.32 (2\sigma)$, due to radiogenic contributions from ^{40}K decay in old North American crustal source rocks that have relatively high K/Ca ratios (cf. Marshall & DePaolo 1989). These data support the results of our gravimetric experiments and indicate that we can detect small radiogenic enrichments at the ϵ -unit level.

Differentiated achondrites (meteorites without relic nebular components, i.e., chondrules) yield initial $\epsilon_{40/44}$ values that are indistinguishable from Earth and Mars. Primitive undifferentiated

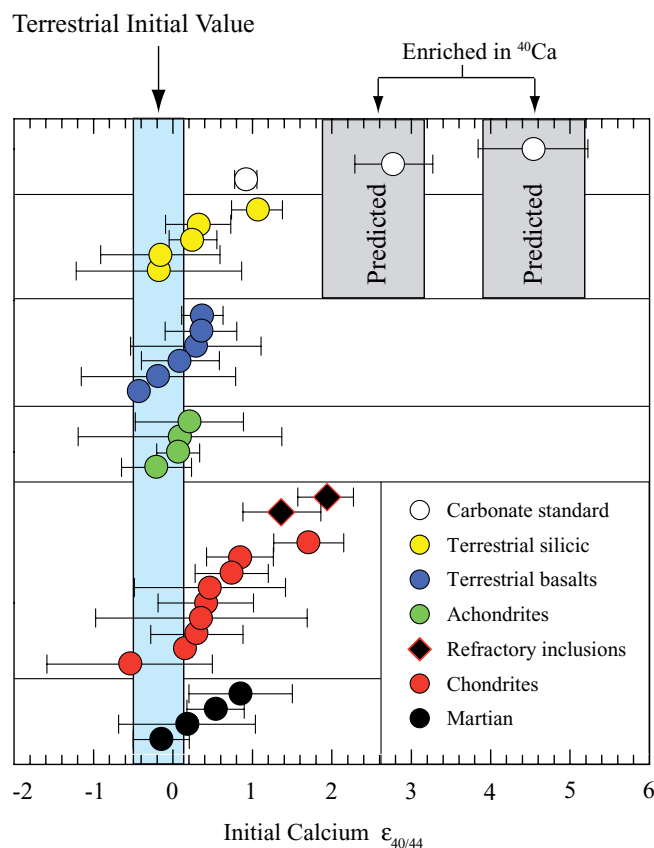


Figure 1. Summary of non-mass-dependent calcium isotopic compositions for a range of planetary materials. At the bulk rock scale most planetary materials initially had similar calcium isotopic compositions. Small excesses relative to Earth (\equiv zero) in initial $\epsilon_{40/44}$ (parts per 10,000) exist among chondrites and refractory inclusions. Earth's initial calcium isotopic composition is defined by the composition of oceanic basalts and differentiated meteorites with an uncertainty of less than ± 30 ppm (SD). An Eocene granite, two Oligocene rhyolites, several mafic lavas including one continental basalt, and a couple Martian samples show slightly elevated $\epsilon_{40/44}$ that are likely due to radiogenic contributions from K-rich sources (Precambrian samples with large measured excesses are not shown, see Table 1). Results from isotopically doped standards used in gravimetric tests are shown for reference (see text). Uncertainties are 2σ and shown if larger than symbol size.

ated chondrites exhibit more variable $\epsilon_{40/44}$ values that range from initial Earth-like values to 1.70ϵ -unit excesses. Of the measured Martian meteorites, two yield $\epsilon_{40/44}$ similar to bulk Earth initial and two do not. The exceptions are the ancient ALH84001 (4550 Ma; Nyquist et al. 1995) and the younger QUE94201 (327 Ma; Borg et al. 1997), both of which have slightly elevated $\epsilon_{40/44}$ values of $0.59 \pm 0.36 (2\sigma)$ and $0.88 \pm 0.65 (2\sigma)$, respectively. This observation is the subject of ongoing study; we worked with unleached samples and therefore the slight excesses may be due to an unrecognized secondary alteration process on Mars or Earth (cf. Borg et al. 1997). Alternatively excess ^{40}Ca may indicate a Martian source component with elevated K/Ca.

Because the measured $^{40}\text{Ca}/^{44}\text{Ca}$ ratios are normalized to a constant value of $^{42}\text{Ca}/^{44}\text{Ca}$, the variable chondrite $\epsilon_{40/44}$ values could be due to either a relative excess of ^{40}Ca or ^{44}Ca , or a relative deficit of ^{42}Ca . After normalization and accounting for radioactive decay, three chondrites and both refractory inclusions show resolvable effects in ^{40}Ca abundances. Four of the chondrites, an inclusion, and two basalts (one from Mars and

Table 1
Calcium Isotope Compositions of Planetary Materials

Sample	Material	<i>n</i>	Age (Ma)	K/Ca _{atomic}	$\epsilon_{40/44}$	$\epsilon_{40/44}^a$	2 σ	$\epsilon_{43/44}$	2 σ
Terrestrial Rocks									
<i>Felsic</i>									
DM-10	Precambrian granitoid	3		...	3.24	...	0.24	0.04	0.82
81-AZ-WG-1	Granite	4	47	1.74	1.12	1.07	0.32	0.06	1.20
Tsm-7	High-silica rhyolite	5	28	3.40	0.38	0.32	0.41	0.29	0.70
Fish Canyon Tuff	Crystal-rich rhyolite	4	28	0.68	0.28	0.27	0.30	0.14	1.55
83-IB-1	Granodiorite	2	120	0.68	-0.03	-0.04	0.75	-0.06	1.49
83-IB-12	Tonalite	2		0.25	-0.15	-0.16	1.04	-1.02	1.54
<i>Mafic</i>									
BCR-1	Continental basalt	5	16	0.488	0.37	0.37	0.26	0.07	0.39
BMR-10	Island arc basalt	2		0.031	0.29	0.29	0.82	0.08	0.31
519-8-3	Pacific MORB	5	12	0.002	0.36	0.36	0.45	-0.07	0.57
519-9-5	MORB	3		0.006	0.08	0.08	0.49	0.30	0.26
NM5087	Atlantic MORB	3		0.004	-0.19	-0.19	0.97	0.32	0.56
SRO-4.50-3.55	Hawaiian tholeiite	4		0.007	-0.43	-0.43	1.13	-0.15	0.68
Meteorites									
<i>Achondrites</i>									
Zagami	Basaltic shergottite	3	185	0.008	0.18	0.18	0.86	0.55	0.99
QUE94201	Basaltic shergottite	3	327	0.001	0.88	0.85	0.65	-0.37	0.68
ALH84001	Martian "diogenite"	8	4550	0.005	0.59	0.54	0.36	-0.54	0.50
EETA7900A	Basaltic shergottite	5	185	0.003	-0.15	-0.15	0.41	-0.26	0.96
Juvinas	Eucrite	4	4539	0.005	0.09	0.03	0.27	0.09	0.46
Angra dos Reis	Angrite	4	4550	0.001	-0.21	-0.22	0.44	0.26	0.73
Bilanga	Diogenite	2	4550	0.005	0.26	0.21	0.68	-0.37	1.20
Norton County	Aubrite	4	4550	0.008	0.16	0.05	1.28	-0.08	0.48
<i>Chondrites</i>									
Murchison	Carbonaceous (CM2)	8	4566	0.036	0.84	0.42	0.60	-0.35	0.63
Murray	Carbonaceous (CM2)	3	4566	0.013	0.33	0.15	0.09	1.83	1.23
Allende	Carbonaceous (CV3)	12	4566	0.015	0.52	0.29	0.58	0.15	0.29
Vigarano	Carbonaceous (CV3)	3	4566	0.013	0.99	0.83	0.42	0.36	0.22
Abee	Enstatite chondrite (EH4)	4	4566	0.092	1.43	0.35	1.33	-0.72	0.90
Dhajala	Ordinary chondrite (H3)	5	4566	0.049	2.28	1.70	0.44	0.37	0.46
Paragould	Ordinary chondrite (LL5)	6	4566	0.063	1.20	0.46	0.95	0.22	0.55
St. Severin	Ordinary chondrite (LL6)	3	4566	0.033	1.13	0.74	0.46	0.69	0.47
Bruderheim	Ordinary chondrite (L6)	4	4566	0.035	-0.12	-0.54	1.04	-0.80	0.32
Refractory Inclusions									
Igneous CAI	Allende	3	4567	...	1.94	1.94	0.35	1.80	1.14
Igneous CAI	Allende (HB1)	3	4567	...	1.36	1.36	0.49	1.34	2.01
Standards and Reference Materials									
DM-40	Precambrian granitoid	3		...	29.32	...	1.96	-0.82	1.13
SRM915A	Carbonate standard	17		...	0.93	...	0.14	-0.30	0.38
SRM915A (+2.5)	Carbonate + radiogenic Ca	3		...	2.77	...	0.49	-0.13	0.99
SRM915A (+5.0)	Carbonate + radiogenic Ca	3		...	4.54	...	0.69	-0.42	0.70
Long-Term Reproducibility of SRM915A									
		<i>n</i>				$\epsilon_{40/44}$	2 SD	$\epsilon_{43/44}$	2 SD
SRM915A	2006 Jul to 2007 Mar	18			0.68	2.28	0.00	1.98	
SRM915A (this study)	2007 Jun to 2007 Nov	17			0.93	0.61	-0.30	1.65	
SRM915A (this study) ^b	2007 Jun to 2008 Oct	27			0.83	0.89	-0.17	1.50	
SRM915	2006 Jul to 2008 Oct.	45			0.80	1.58	-0.13	1.68	

Notes.

Data normalized to $^{42}\text{Ca}/^{44}\text{Ca} = 0.31221$ then calibrated to average of multiple standard measurements for each analytical session. Epsilon values $\epsilon_{4x/44} = \ln(R_{\text{spl}}/R_{\text{ref}}) \times 10^4$ where R_{ref} is either $^{40}\text{Ca}/^{44}\text{Ca} = 47.1487$ or $^{43}\text{Ca}/^{44}\text{Ca} = 0.064868$ that correspond to the preferred $^{40}\text{Ca}/^{42}\text{Ca}$ value of 151.016 (Marshall & DePaolo 1989; Russell et al. 1978). n = number of replicate measurements. Unless stated otherwise, uncertainties are 2σ . The statistics of small numbers may behave differently than standard errors. In order to account for this difference a good approximation for 95% conf. intervals is to multiply the standard errors by the Student's t -adjustment (Mahon 1996). For samples that have been replicated ≤ 3 times, this can lead to a substantial (and in this case unrealistic) increase in uncertainty. Five or more replicates of each sample would be ideal, but impractical for typical TIMS measurements. Nevertheless, clear differences among bulk samples at the 95% conf. level can be seen among EETA7900A -0.15 ± 0.65 ($n = 5$), Murchison 0.84 ± 0.74 ($n = 8$), and Dhajala 2.28 ± 0.70 ($n = 5$) in which their standard errors have been multiplied by the Student's t -adjustment. Ages and K/Ca compositions of meteorites come from Jarosewich (1990), Kallemeyn et al. (1989), Laul et al. (1986), Mittlefehldt (1994), Mittlefehldt & Lindstrom (1990), Shih et al. (1993), Stolper & McSween (1979), von Michaelis et al. (1969), and Warren et al. (1999). Igneous rocks from Earth include the following: DM-40 and DM-10 evolved marginal members of the Precambrian Muskox layered intrusion; 81-AZ-WG-1 a Late Cretaceous peraluminous muscovite-bearing granite from the Santa Catalina Mountains of southern Arizona (Farmer & DePaolo 1984); Tsm-7 a strongly welded vitric crystal-poor rhyolitic Tertiary ignimbrite from the early Sapinero Mesa Tuff collected from its type locality near its source the San Juan and Uncompahgre caldera complex, western San Juan volcanic field, Colorado (Simon 2000); Fish Canyon Tuff a slightly welded plagioclase sanidine hornblende quartz crystal-rich Tertiary dacitic ignimbrite collected in Saguache Creek, Colorado some tens of km from its source the La Garita caldera, central San Juan volcanic field (Whitney & Storrer 1985); 83-IB-1 and 83-IB-12 biotite and hornblende-bearing granodiorites from central and northeastern Oregon, respectively (Marshall & DePaolo 1989); BCR-1 a well characterized U.S. Geological Survey standard of Columbia River Basalt, Oregon (Gladney et al. 1983); 519-8-3 and 519-95 massive tholeiitic normal-type mid-ocean ridge basalts, dredged from the South Atlantic ridge during the Deep Sea Drilling Project Leg 73 (Dietrich et al. 1984); BMR-10 a relatively coarse-grained plagioclase and clinopyroxene phyric basalt from Mount Bangum a Quaternary volcano in the New Britain island arc of Papua New Guinea (DePaolo & Johnson 1979); NM5087 a plagioclase phyric massive tholeiitic normal-type mid-ocean ridge basalt flow unit dredged from the North Atlantic ridge during the expedition at 22° - 23° north (Hemond et al. 2006; Melson et al. 1968); and SRO-4.50-3.55 a massive tholeiitic ocean island basalt flow unit collected at Mauna Kea volcano by the Hawaiian Scientific Drilling Program from 1083.7 m depth (Rhodes & Vollinger 2004).

^a Age-corrected values.

^b Overall external reproducibility of standard (i.e., not including sample-standard bracketing) for samples reported herein that reflects the effects of replacing the Faraday cup liners and modifying the cup configuration (i.e., from measuring four isotopes of calcium to all six isotopes, see text).

one from Earth) also exhibit apparent ^{43}Ca effects. The apparent ^{43}Ca effects in the planetary samples are not much larger than their associated 2σ uncertainties and may be analytical artifacts resulting from averaging among a small number of replication analyses. There are, however, samples that are clear outliers, e.g., carbonaceous chondrite Murray and one of the refractory inclusions (see Table 1). The minimal degree of variation in $\varepsilon_{43/44}$ for many samples suggests that the isotopes ^{42}Ca , ^{43}Ca , and ^{44}Ca are present in proportions that are similar to terrestrial after normalization to a constant $^{42}\text{Ca}/^{44}\text{Ca}$. Hence, the positive values of $\varepsilon_{40/44}$ in the primitive meteorites are likely due to either a relative excess of ^{40}Ca , or a depletion of the three other isotopes in proportions that for the most part preserve the terrestrial isotope ratios after normalization. The excess ^{43}Ca observed in the refractory inclusions provide evidence that material with exotic proportions of the light calcium isotopes existed in the early solar system. It is possible that the excess ^{43}Ca in Murray indicates that the bulk sample split used in this study had a greater proportion of primitive material, e.g., refractory inclusions. Nevertheless, the apparent excess of ^{40}Ca in nearly all of the chondritic meteorite samples indicates that they contain more of a particular nucleosynthetic component than do small differentiated planetary bodies, Earth, and Mars.

There are previous calcium isotope analyses of bulk rock meteorites in the literature. Shih et al. (1993) reported $^{40}\text{Ca}/^{44}\text{Ca}$ ratios for four eucrites, two shergottites, and several lunar rocks, and found no resolvable differences (at the ~ 1.2 ε -unit level) from terrestrial standards. Their value for Shergotty appears to have a slightly high $\varepsilon_{40/44}$, similar to what we have measured for Martian meteorites ALH84001 and QUE94201. Samples reported in Russell et al. (1978) were spiked with a tracer solution of enriched ^{42}Ca and ^{48}Ca and showed a total variation of $\varepsilon_{40/44}$ of about 24 ε -units in meteorites. This variation was attributed entirely to mass-dependent fractionation. However, small deficits in ^{40}Ca are difficult to distinguish from mass-dependent effects in samples that are spiked with a ^{42}Ca – ^{48}Ca mixture, unless there are also high-precision data for the $^{43}\text{Ca}/^{44}\text{Ca}$ ratio. The Russell et al. (1978) measurements of $^{43}\text{Ca}/^{44}\text{Ca}$ are not sufficiently precise to evaluate non-mass-dependent effects at the level we have measured them. Although we have not measured lunar samples, the previous results (Russell et al. 1978; Shih et al. 1993) suggest that there is no difference between terrestrial and lunar calcium, which would be consistent with oxygen isotopic data (e.g., Clayton et al. 1973b).

3. COMPARISONS TO NUCLEOSYNTHETIC MODELS

It is most likely that the observed isotopic effects in chondrites stem from calcium produced in different nucleosynthetic events and not completely homogenized by processes in the solar nebula before the chondrite parent bodies formed. Understanding the degree of initial isotope heterogeneity is critical for accurate interpretation of short-lived radionuclides, such as ^{26}Al ($^{26}\text{Mg}^*$), ^{53}Mn ($^{53}\text{Cr}^*$), ^{60}Ni ($^{60}\text{Fe}^*$), ^{146}Sm (^{142}Nd), and ^{182}Hf (^{182}W) (e.g., Bizzarro et al. 2005; Boyet & Carlson 2005; Kleine et al. 2004; Lugmair & Shukolyukov 1998; Shukolyukov & Lugmair 1993; Yin et al. 2002b) that have been used to date condensation, accretion, and differentiation of rocky materials within the first ~ 50 Ma of the solar system. There is evidence from study of presolar grains and CAIs that materials from both asymptotic giant branch (AGB) stars and from supernovae (SNe) were added to the solar nebula (e.g., Alexander & Nittler 1999; Nittler et al. 1996, 2008). Evidence for elevated abundances

of short-lived radionuclides attest to the fact that freshly synthesized elements were added at the time and possibly related to an event that caused molecular cloud collapse (MCC; e.g., Cameron & Truran 1977). It is more difficult to know whether the addition of stable nuclides was dominated by freshly synthesized elements or from local recycled interstellar material. In AGB stars the isotopes ^{42}Ca , ^{43}Ca , and ^{44}Ca can be made in excess and in approximately terrestrial (or solar) proportions, as they are produced in the He-burning zones of massive stars (e.g., Weaver & Woosley 1993). Under the same conditions, ^{40}Ca would be depleted by a large factor. Hence blowoff from an AGB star would tend to have calcium that would show a relative deficit of ^{40}Ca when normalized to solar $^{42}\text{Ca}/^{44}\text{Ca}$.

If the calcium isotopic composition of the solar system reflects a combination of nucleosynthetic sources then blow off of material with large ^{40}Ca depletions would require admixture with material with ^{40}Ca excesses. The slight ^{40}Ca excesses observed in many of the chondrites could represent such sources, counterbalancing the predicted deficits of ^{40}Ca produced in AGB stars. Models for nucleosynthesis in Type II SNe indicate that calcium isotopes can be produced in widely varying proportions depending on stellar mass, the details of the explosion (Rauscher et al. 2002) and the injection mass cut (Meyer & Clayton 2000). Therefore material ejected from SNe could produce both relative deficits and/or the excesses of ^{40}Ca that when normalized to solar $^{42}\text{Ca}/^{44}\text{Ca}$ are similar to those reported here.

Any specific mixture of nucleosynthetic components that is used to explain the calcium isotope effects has implications for other refractory elements. To evaluate whether the observed effects in ^{40}Ca , ^{50}Ti , ^{135}Ba , ^{142}Nd and ^{144}Sm can be accounted for by mixtures of likely nucleosynthetic components, we compare the calculated isotope effects based on stellar models to those measured in chondrites. This comparison is complicated by the number of variables inherent in the stellar models and the fact that all of the measured isotopic ratios are normalized, but there are enough consistencies that some preliminary conclusions can be drawn.

Equation (1) shows how the relative abundance of isotope i (i.e., in a chondrite $N_{i,\text{ch}}$) can be calculated by subtracting a small fraction (F) of a nucleosynthetic yield from a model solar system:

$$N_{i,\text{ch}} = N_{i,\text{ss}} - (N_{i,\text{SNe}} \pm N_{i,\text{SNe}}^*)F, \quad (1)$$

where $N_{i,\text{ss}}$ is the total abundance of isotope i in the solar system, $N_{i,\text{SNe}}$ is the abundance of the stable nuclide i , and $N_{i,\text{SNe}}^*$ is the abundance of i added from a radioactive progenitor (i.e., due to ^{146}Sm decay to ^{142}Nd and ^{44}Ti decay to ^{44}Ca). The relative abundances of each isotope for a model solar system can be found in Anders & Grevesse (1989), which are tabulated as mass fractions in Table 7 of Rauscher et al. (2002). The nucleosynthetic mass yields for all stable nuclei and their radioactive progenitors in explosions of Type II SNe of Rauscher et al. (2002) and unpublished yields for AGB stars provided by A. Davis and R. Gallino are used. Once $N_{i,\text{ch}}$ of each isotope is determined it is normalized to the abundance of the reference isotope ($N_{\text{ref},\text{ch}}$)

$$R_{i/\text{ref},\text{ch}} = (N_{i,\text{ch}}/N_{\text{ref},\text{ch}}), \quad \text{e.g., } ^{40}\text{Ca}/^{44}\text{Ca}. \quad (2)$$

The abundance $N_{\text{ref},\text{ch}}$ is also calculated from Equation (1) and chosen by convention. For comparison purposes isotope ratios are corrected (using the exponential law) so that the value of the normalizing isotope ratio (e.g., $R_{j/\text{ref},\text{ch}} = ^{42}\text{Ca}/^{44}\text{Ca}$) is equal to the accepted model solar system value ($R_{j/\text{ref},\text{ss}}$).

The fractionation-corrected ratios ($R_{i/\text{ref},\text{ch}}^{\text{cor.}}$) are obtained from Equations (3) and (4):

$$R_{i/\text{ref},\text{ch}}^{\text{cor.}} = R_{i/\text{ref},\text{ch}} / (\text{atw}, i / \text{atw}, \text{ref})^P \quad (3)$$

$$P = \frac{\ln(R_{j/\text{ref},\text{ch}} / R_{j/\text{ref},\text{ss}})}{\ln(\text{atw}, j / \text{atw}, \text{ref})}, \quad (4)$$

where atw, i and atw, ref are the atomic weights of each corresponding isotope and P is the fractionation factor. Note that $R_{j/\text{ref},\text{ss}}$ assumes the relative abundances given in the model solar system of Rauscher et al. (2002) and therefore the normalizing $^{42}\text{Ca}/^{44}\text{Ca}$ ratio is 0.30847 rather than the nominal value of 0.31221. Corrected ratios once converted to epsilon notation are used to calculate slopes that can be compared to the effects in chondrites (see Figure 2).

The small measured ^{40}Ca excesses measured in chondrites correlate to some degree (Figures 2(a) and (b)) with published ^{142}Nd deficits (Andreasen & Sharma 2006; Boyet & Carlson 2005; Carlson et al. 2007). Virtually all chondritic meteorites have depletions in ^{142}Nd of between ~ 20 and 40 ppm relative to Earth. There is also a systematic ^{142}Nd depletion of ~ 10 –15 ppm between carbonaceous and enstatite chondrites and the ordinary chondrites, which has been interpreted by Andreasen & Sharma (2007) and Carlson et al. (2007) to reflect distinct nucleosynthetic components and not radioactive decay of ^{146}Sm . Correlated ^{142}Nd depletions and ^{40}Ca excesses in the approximate proportions observed are expected if the solar system reflects a mixture of material represented by the (age-corrected) chondrites and material derived from 15–25 M_{\odot} SNe (Rauscher et al. 2002). Figure 2(c) shows the predicted effects for all calcium and neodymium isotopes for mixtures involving SNe (Rauscher et al. 2002) and AGB stars (provided by A. Davis and R. Gallino). Calculations show that collateral effects based on SNe mass yields for 15 and 21 M_{\odot} stars (S15 and S21) are consistent with measured values, i.e., normal within uncertainties (e.g., the gray band of the inset shows acceptable variability in $^{145,150}\text{Nd}$). The ^{40}Ca and ^{43}Ca excesses predicted for SNe mass yields for S15 are consistent with the refractory inclusions (see Table 1). Correlated ^{142}Nd depletions and ^{40}Ca excesses would also be expected for mixtures of solar system material and blow-off from a nearby AGB star (Busso et al. 2003; Nittler 2003). However the magnitude of the ^{142}Nd effect for the AGB models is ≥ 10 times the ^{40}Ca effect, which means that the observed ^{142}Nd effects should correspond to undetectable (about 1–2 ppm) shifts in ^{40}Ca (compare Figures 2(a) and (b)). Likewise collateral effects in $^{145,150}\text{Nd}$ for 2–3 M_{\odot} AGB stars exceed those reported. Accounting for some radiogenic ingrowth of ^{142}Nd and ^{40}Ca , the ordinary chondrites can be explained entirely by variable amounts of SNe addition. In contrast, a solar composition that includes admixture of carbonaceous chondrite source components appears to require multiple stellar sources, perhaps both AGB and SNe additions. Models that invoke solar system heterogeneity derived solely from an AGB admixture are not compatible with the existence of ca. 50–150 ppm ^{40}Ca excesses. Comparable models of AGB yields for titanium, samarium, and barium would help constrain these conclusions, but are not available. Most, but not all of our data are incompatible with just addition of AGB sources.

If the small ^{40}Ca variations we have measured reflect residual solar system heterogeneity, then the ^{142}Nd variations may also be due, in part, to initial isotopic heterogeneity and not simply to radioactive decay of the short-lived ^{146}Sm isotope (Boyet &

Carlson 2005; Rankenburg et al. 2006). The ^{142}Nd differences could be due to variations in the abundance of ^{146}Sm in the solar nebula, a possibility that is made more likely by the discovery of variations in the p -process isotope ^{144}Sm in meteorites (Andreasen & Sharma 2006). This conclusion is also consistent with the observed barium isotopic differences between chondritic meteorites and the Earth (Andreasen et al. 2008; Carlson et al. 2007; Ranen & Jacobsen 2006). Although there are few data to evaluate whether the ^{135}Ba , ^{142}Nd , and ^{144}Sm variations correlate in the expected manner, Figures 2(e)–(h) show how these data, along with our calcium isotope data, compare to mixing models based on the mass yield calculations of Rauscher et al. (2002). In general the ordinary chondrites match calculated mixing curves for SNe mass yields (S15 and S21) fairly well. The fit is improved if the initial $\epsilon_{40/44}$ of the solar system is closer to the -0.5 value of ordinary chondrite Bruderheim. The effects shown by the carbonaceous chondrites share similarities with the mixing calculations, but in some cases the fits are less satisfying. Because the effects are not much larger than the long-term reproducibility of any of the isotopic measurements, the miss-fits could suggest that there are unrecognized issues related to analysis of calcium and/or one of the other elements. Alternatively, this may reflect decoupled nucleosynthetic sources as has been suggested by Andreasen & Sharma (2007) and Carlson et al. (2007) and/or a need to improve nucleosynthetic production models of SNe explosions.

If the ^{142}Nd enrichment for the Earth is not entirely due to radioactive decay of ^{146}Sm , then it would loosen the requirement for a hidden low-Sm/Nd reservoir in the Earth (Boyet & Carlson 2005; Rankenburg et al. 2006). The measured calcium and neodymium isotopic differences show that the initial composition of the Earth is distinct from many chondrites, and as such strengthens interpretations that the early solar system was isotopically heterogeneous. Even if some of the variability in ^{142}Nd is due to solar system heterogeneity, some radioactive ingrowth of ^{142}Nd is probably required because the predicted shifts in ^{142}Nd corresponding to the measured ^{40}Ca , ^{144}Sm , and $^{135,137}\text{Ba}$ heterogeneities are not large enough to explain all of the observed ^{142}Nd differences.

The increasingly detailed geochronology available for the early solar system allows us to put our results into a rough chronological context. The beginning of the solar system is dated by the age of CAIs in chondrites, which is 4.567 billion years ago (Amelin et al. 2002; Bouvier et al. 2007). The CAIs probably formed within 10^5 years of the beginning of MCC and are the oldest known solid materials in the solar system (see Montmerle et al. 2006). Chondrules, the distinguishing petrological feature of chondritic meteorites, appear to have formed up to 2 million years after CAI formation (Connelly et al. 2008), but possibly less according to Simon et al. (2005) and Moynier et al. (2007). The mean time of accretion of the Earth is believed to be in the range of 20–40 million years after CAI formation; Mars may have accreted earlier (cf. Nimmo & Kleine 2007). Our observations suggest that there was still residual calcium isotope heterogeneity in the solar system for 2 million years, but it was gone by 20–40 million years after formation of CAIs (see Figure 3). The implication is that CAIs should show more calcium isotopic heterogeneity than bulk chondrites. This has not yet been fully tested, but our measurements are consistent with this interpretation. Notably the measurements of Niederer & Papanastassiou (1984; but see Jungck et al. 1984) indicate that some CAIs have $\epsilon_{40/44}$ values (when their data are renormalized appropriately) that vary from -34 to $+38$ ϵ -units,

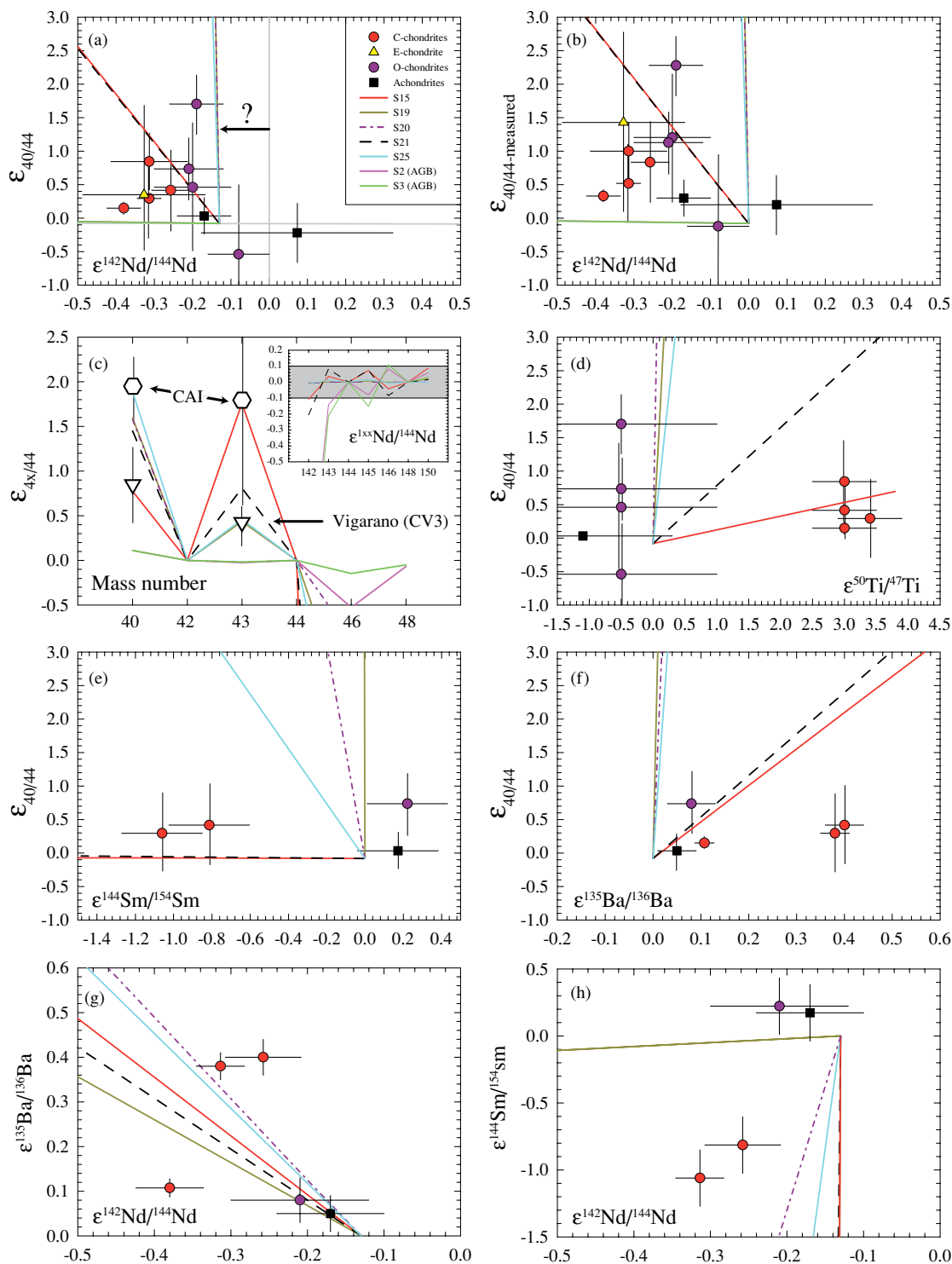


Figure 2. Agreement of chondrite measurements and nucleosynthetic mixing trends for isotopes of refractory elements. Note that symbols and model curves are defined in panel (a) and used consistently throughout. Panel (a) shows the relative enrichments in ^{40}Ca and relative depletions in ^{142}Nd (Andreasen & Sharma 2007; Boyet & Carlson 2005; Carlson et al. 2007) compared to terrestrial after age correction (see text). Average ordinary chondrite ^{142}Nd value assumed for Paragould. Arrow shows an estimated age correction (10–20 ppm) in ^{142}Nd for ingrowth of Earth relative to chondrites suggested by Andreasen & Sharma (2007) and Carlson et al. (2007). Panel (b) shows measured ^{40}Ca excesses and ^{142}Nd depletions. Panel (c) shows relative collateral effects among calcium isotopes for mixing trends (the inset shows relative collateral effects among neodymium isotopes for the given magnitude of calcium effects). Data for a refractory inclusion and carbonaceous chondrite Vigarano included for comparison. Panel (d) shows enrichments in ^{40}Ca and effects in ^{50}Ti (Leya et al. 2008). Single titanium value of ordinary chondrite Forest Vale assumed to be representative. Average carbonaceous chondrite ^{50}Ti value assumed for Murchison, Murray, and Vigarano. Panel (e) shows enrichments in ^{40}Ca and effects in ^{144}Sm (Andreasen & Sharma 2006). Panel (f) shows enrichments in ^{40}Ca and enrichments in ^{135}Ba (Andreasen & Sharma 2007; Carlson et al. 2007). Panel (g) shows enrichments in ^{135}Ba and depletions in ^{142}Nd . Panel (h) shows relative effects in ^{144}Sm and ^{142}Nd . Mixing trends derived from subtraction of isotopic abundances in model nucleosynthetic mass yields from terrestrial-based estimate of the initial composition of the solar system (see text). Nucleosynthetic yields used for SNe come from Rauscher et al. (2002) and for AGB stars based on Busso et al. (2003) and unpublished results provided by A. Davis and R. Gallino. The correlations suggest that ^{142}Nd effects may partially originate from initial nebular heterogeneity. In general, chondrites match calculated trends that assume the solar system had contributions from SNe mass yields (S15 red and S21 black-dashed curves). The fit between the mixing trends and the effects shown by the carbonaceous chondrites imply a mixture of stellar components. Uncertainties are 2σ .

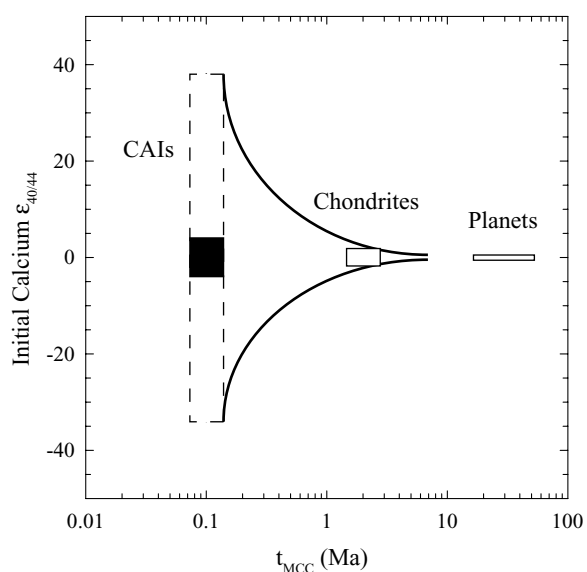


Figure 3. Time scale for homogenization of calcium isotopes in the protoplanetary disk, beginning with MCC. The calcium isotope data for CAIs come from this study ($n = 2$) and Jungck et al. (1984) and Niederer & Papanastassiou (1984). Chondrite and planetary data are from this study. Filled region indicates range of normal CAI compositions. Black outline shows the general sense of homogenization with time.

at least 20 times larger than those measured here, although most have values between -4 and $+4$ ϵ -units.

4. CONCLUSIONS

The accumulating evidence for both stable isotope and short-lived isotope variations between meteorites and terrestrial planets suggests that there were significant spatial and/or temporal heterogeneities in the early solar nebula. In most cases the magnitude of the effects is small and their discovery has required an unprecedented level of analytical precision and method development. The available data suggest that refractory matter in meteorites records a combination of nucleosynthetic sources in which contributions from relatively low mass SNe were important.

The question first posed by Clayton et al. (1973a) for oxygen isotopes is how to preserve nucleosynthetic heterogeneity in the early solar nebula long enough for it to be evident in planetary bodies. Recent models suggest that radial mixing within the protoplanetary disk can be sufficiently rapid to completely homogenize the nebula on the time scale of planetesimal formation (10^5 – 10^6 years), while still allowing heterogeneity to be recorded by the earliest solid solar system materials such as CAIs (Boss 2006). The results for refractory elements, including those for calcium isotopes presented here, are largely consistent with these mixing models. They suggest, however, that the time scale for nebular mixing may be similar to, rather than much shorter than, the time scale of the planetesimal formation, or that there were continuing late contributions to the nebula from external sources as planetesimals were forming. The similarity in calcium isotope composition of differentiated parent bodies, as represented by the Earth, Mars and ordinary chondrites, indicates that isotopic homogenization for refractory elements was essentially complete by the time the inner solar system planets were fully formed. This latter observation, and those for other refractory elements studied so far, suggest that the total mass of late, nucleosynthetically distinct additions to the solar nebula was small.

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