Stable strontium isotopic heterogeneity in the solar system from double-spike data

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Abstract

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Strontium isotopic anomalies in meteorites are important in assessing nucleosynthetic sources to, and measuring the timing of, early solar system processes. However, conventional use of a constant $^{88}Sr/^{86}Sr$ value in correcting for instrumental mass fractionation during analysis renders measurements ambiguous and removes information on mass-dependent fractionation variations. From double-spike techniques we obtain data for the four stable strontium isotopes free of this ambiguity, and report measurements from a range of meteoritic, lunar and terrestrial materials. The Earth, Moon, basaltic eucrites and feldspars from angrites (differentiated samples) follow a single mass-dependent fractionation line and have a common nucleosynthetic origin in terms of their strontium isotopes. In contrast, bulk rock CI, CV3, CM and CO chondrite samples serve to define another mass-dependent fractionation line, displaced by 94 ± 28 ppm to heavier $^{84}Sr/^{86}Sr$ and/or $^{88}Sr/^{86}Sr$ ratios than that for the differentiated samples. Our Sr-isotopic data are consistent with a primary contrast in early solar system composition between an outer zone of primitive, mostly undifferentiated, materials and an inner zone of (almost entirely) differentiated materials that accumulated to form the terrestrial planets.

Introduction

Isotopic anomalies in extraterrestrial materials hold the keys to disentangling the origins and development of the early solar system (Dauphas and Schauble, 2016; Qin and Carlson, 2016, for recent overviews). Stable strontium isotopes in particular are critical in discerning the nucleosynthetic origins of early solar system components and the timing of accretion processes. Furthermore, variations caused by high temperature mass-dependent fractionation (Young *et al.*, 2002) are also important (Patchett, 1980a,b; Moynier *et al.*, 2010; Charlier *et al.*, 2012) in providing insights into nebular and accretionary processes.

Disentangling strontium isotopic variations is problematic, however, through a first order analytical issue. Virtually all TIMS measurements of strontium isotopes employ a fixed $^{88}Sr/^{86}Sr$ ratio (8.375209) to correct for instrumental mass fractionation (IMF) during analysis (Papanastassiou and Wasserburg, 1969, 1978; Moynier *et al.*, 2010; Charlier *et al.*, 2012; Hans *et al.*, 2013). However, adoption of this fixed value precludes investigation of mass-dependent variations in the stable isotopes. In comparison, MC-ICP-MS techniques using either Zr-normalisation and/or sample-standard bracketing

(Moynier *et al.*, 2010; Charlier *et al.*, 2012) can yield $^{88}Sr/^{86}Sr$ and $^{87}Sr/^{86}Sr$ ratios to examine mass-dependent fractionation effects, but cannot accurately measure $^{84}Sr/^{86}Sr$ due to ^{84}Kr interference. Most published Sr isotopic data are collectively hamstrung by one or other of these issues.

Here we present TIMS data obtained using a double-spike methodology (Rudge *et al.*, 2009) that, in contrast, recovers the abundance of the four Sr isotopes, free from any normalisation assumption (see Supplementary Information). We have measured Sr isotopes in a suite of terrestrial, lunar, and undifferentiated and differentiated meteorite samples (Table S-1). We undertook two determinations on each sample: an unspiked measurement that is IMF-corrected and a spiked measurement which, in combination with the unspiked analysis, permits us to deconvolve the absolute ratios of $^{84}Sr/^{86}Sr$, $^{88}Sr/^{86}Sr$ and $^{87}Sr/^{86}Sr$, independent of any fixed IMF correction (Neymark *et al.*, 2014). Because the uncertainties associated with the values used to derive the isotopic ratios are highly correlated, we have also considered the individual errors associated with each measurement and propagated these to derive robust error estimates (Supplementary Information).

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Results and Discussion

Sr isotopic results from double spike data. We present our data in three-isotope plots ($\delta^{84/86}$Sr *versus* $\delta^{88/86}$Sr where δ represents ‰ deviation relative to NBS-987). Terrestrial samples (Fig. 1a) form a linear array that lies within error of the calculated equilibrium mass-dependent fractionation line (MDFL) produced by high temperature mass fractionation (Young *et al.*, 2002), and cluster around the bulk silicate Earth value for $\delta^{88/86}$Sr of ~+0.29 ‰ (Moynier *et al.*, 2010; Charlier *et al.*, 2012). Linear regression on our data from all terrestrial, lunar, eucrite, diogenite, and angrite samples yields a line with a slope of -0.981 ± 0.047 (Mean Square of Weighted Deviation; MSWD = 4.1) that is identical within error to the theoretical equilibrium MDFL (slope = -0.978: Young *et al.*, 2002). Our regression line (here labelled the 'terrestrial' MDFL) passes within error of the origin, indicating that these samples and their parent bodies have a nucleosynthetic Sr isotopic composition in common with Earth (and the NBS987 standard, by definition), albeit modified by high temperature mass-dependent fractionation processes (see below). Other meteorite samples show contrasting behaviour, with variations in $\delta^{88/86}$Sr and/or $\delta^{84/86}$Sr, driving the data points away from the 'terrestrial' MDFL towards heavier values (Fig. 1b). Ungrouped achondrites and carbonaceous chondrites (classes CI, CV3, CM) lie significantly to the right of the 'terrestrial' MDFL. There can be defined an apparent second MDFL from the data for the ungrouped achondrites and chondrite classes CI, CV3 and CM, together with the heavy end members of the CO and CK classes (see Table S-1 for the samples used). This second line (labelled the 'offset' MDFL) has a slope of -1.00 ± 0.21; MSWD = 7.5. This 'offset' MDFL is displaced by 94 ± 28 ppm heavier in $\delta^{84/86}$Sr or $\delta^{88/86}$Sr from the 'terrestrial' MDFL (Fig. 1b). There is a spread in the data for the ordinary chondrites and CO and CK undifferentiated samples between the two MDFLs: these data are plotted in Figure 1b, but not used to define the offset MDFL.

In general, the 'terrestrial' and 'offset' MDFLs are defined by differentiated *versus* undifferentiated materials, respectively. However, there are three exceptions to this generalisation. First, the enstatite chondrite (Abee) lies exactly on the 'terrestrial' line, despite its undifferentiated nature. Second, and in contrast, the two anomalous achondrites (NWA 011, NWA 5400) both lie within error of the 'offset' MDFL despite their differentiated nature. NWA 011 similarly plots within the 'carbonaceous chondrite' field in Cr-Ti isotopic space (see Warren, 2011). Third, the diversity seen in the ordinary chondrites and CO and CK undifferentiated samples we infer reflects the mixing within individual samples between components that have been through some kind of processing (falling on the 'terrestrial' MDFL) *versus* those not processed (falling on the 'offset' MDFL). Analysis of individual, physically separated components from these meteorites would be needed to test this inference.

Mass-dependent fractionation processes. From our work we can evaluate unambiguously the extent of mass-dependent Sr isotopic fractionation within the various reservoirs contributing to planetary materials. This can only be achieved through use of the double-spike technique. Equilibrium or kinetic fractionation effects (*e.g.,* Blanchard *et al.,* 2017; Watkins *et al.,* 2017) in the data presented here can be related to two different realms of processes. First, the fractionation that occurred during the development of the components that were assembled to produce the meteorites (regardless of their degree of differentiation). Second, magmatic processes leading to differentiation in newly forming and present-day planetary objects. The influence of 'normal' magmatic processes is seen in the spread in values along the MDFL shown by our terrestrial samples where they cover a range about half that of the entire sample suite.

Mass-independent anomalies. To allow for mass-dependent fractionation and highlight the anomalies due to either *p*-process ^{84}Sr or *r*-process-influenced ^{88}Sr, we recast our data as Δ values, *i.e.* the difference between the true value and the corresponding value along the equilibrium MDFL calculated using the true value for the other isotopic ratio (Fig. 2). If the anomalies are due solely to ^{84}Sr, the departure from the MDFL is horizontal in Figure 1, whereas if the anomaly is solely in ^{88}Sr, the offset is vertical. In practice, the numerical values for Δ^{84}Sr and Δ^{88}Sr so calculated are virtually identical because the MDFL slope is so close to 45° and the line is effectively straight across the range of values reported here. Comparison of our results with published data shows several features. The weighted mean Δ^{84}Sr of our terrestrial samples (assuming that any variation is in ^{84}Sr alone) is -0.0002 ± 0.0083 ‰ 2 s.d. (MSWD = 4.3, n = 51), and that of the terrestrial, lunar, eucrite, diogenite and angrite feldspar samples combined is -0.0018 ± 0.0060 ‰ 2 s.d. (MSWD = 4.1, n = 78), demonstrating that the NBS-987 ^{84}Sr/^{86}Sr composition is not at all anomalous (*cf.* Moynier *et al.*, 2012). Additionally, differences in ^{84}Sr/^{86}Sr proposed between Earth, Moon and enstatite chondrites *versus* eucrites and ordinary chondrites (Moynier *et al.*, 2012) are not seen in our results. It is not clear how such discrepancies have arisen.

If the non-mass-dependent anomalies that we report are considered as reflecting *p*-process variations in ^{84}Sr, then several conclusions can be drawn. The elevated apparent Δ^{84}Sr values we obtain from bulk samples in CI, CV and CM chondrites (Fig. 2) cannot reflect incomplete dissolution of refractory pre-solar SiC grains, with their highly depleted ^{84}Sr (Nicolussi *et al.*, 1998; Podosek *et al.*, 2004; Paton *et al.*, 2013), as such grains are not present in concentrations that would significantly affect the bulk meteorite composition (Moynier *et al.*, 2012; Paton *et al.*, 2013). CV3 chondrites contain less SiC than CM chondrites (Huss *et al.*, 2003), yet we record a similar range in elevated apparent Δ^{84}Sr values. Two dissolutions of Murchison from separate chips of this stone also yield apparent Δ^{84}Sr values that are in close agreement. Moreover, the elevated apparent Δ^{84}Sr values in two ungrouped achondrite samples (Fig. 1b; Supplementary Information, Table S-1) reflect the bulk composition since these differentiated stones are unlikely to contain any surviving pre-solar material (Dauphas and Schauble, 2016).
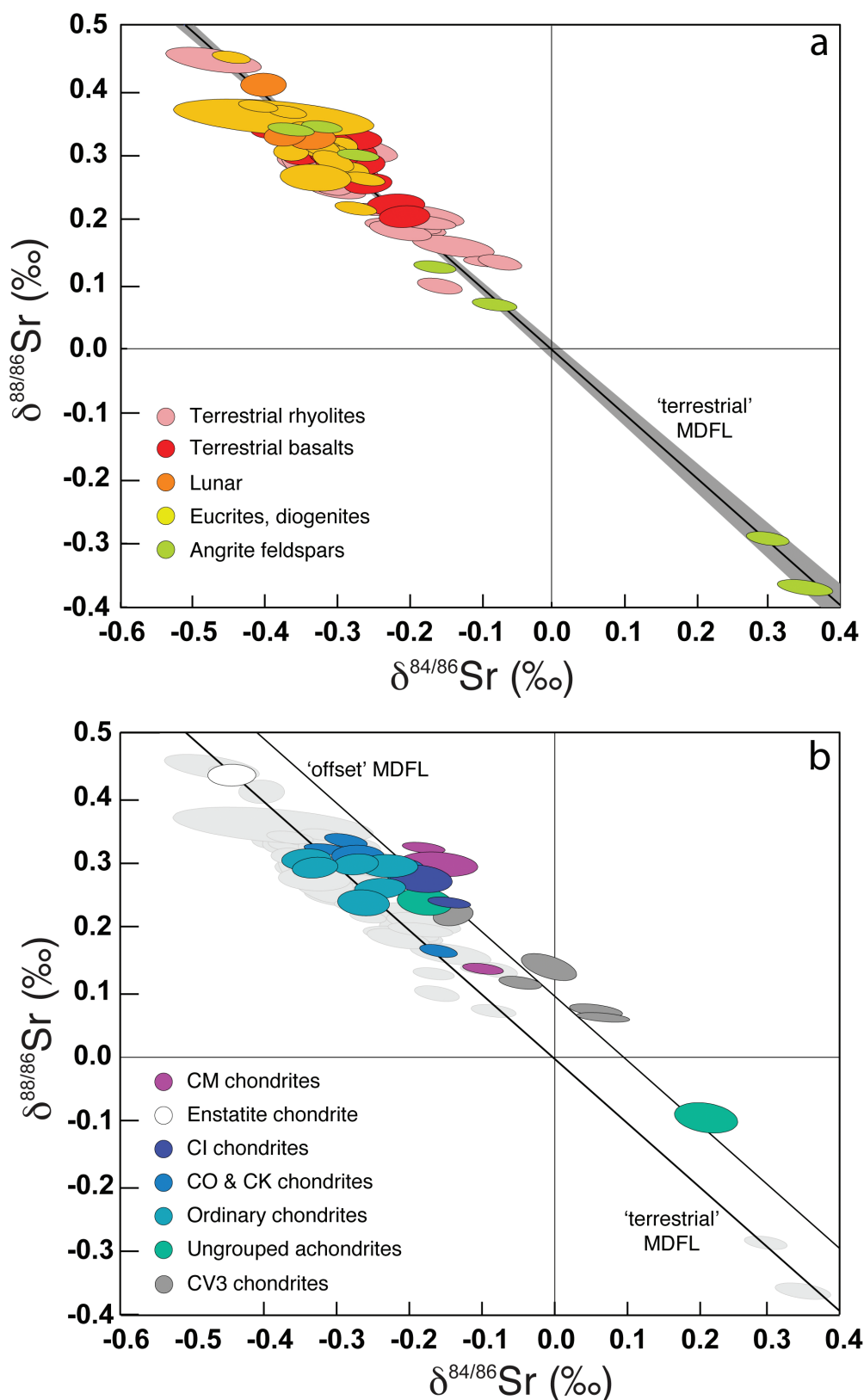
Figure 1 Three-isotope plots of all terrestrial and non-terrestrial data. **(a)** Plot of $\delta^{88/86}Sr$ *vs* $\delta^{84/86}Sr$ showing the data for terrestrial, lunar, eucrite, diogenite and angrite samples in this study (Supplementary Information, Table S-1). MDFL denotes the equilibrium mass-dependent fractionation line which passes through the origin (the assumed composition of NBS-987) with a slope of -0.978 (Young *et al*., 2002). The shaded region is the 2 s.d. error envelope around the line of best fit to the data points plotted; the line itself is analytically and visually indistinguishable from the equilibrium MDFL. Data points are represented by their 2 s.d. uncertainty envelopes calculated using the methods outlined in the Supplementary Information. **(b)** Plot of $\delta^{88/86}Sr$ *vs* $\delta^{84/86}Sr$ showing the data measured in this study. Data points plotted in panel a are greyed out to minimise overlap. We show two lines: a 'terrestrial' MDFL which is the line of best-fit to the data points shown in panel a, and an 'offset' MDFL calculated from ungrouped achondrites and chondrite classes CI, CV3 and CM2, together with the heavy end members of the CO and ordinary chondrite classes (see Table S-2 in Supplementary Information).
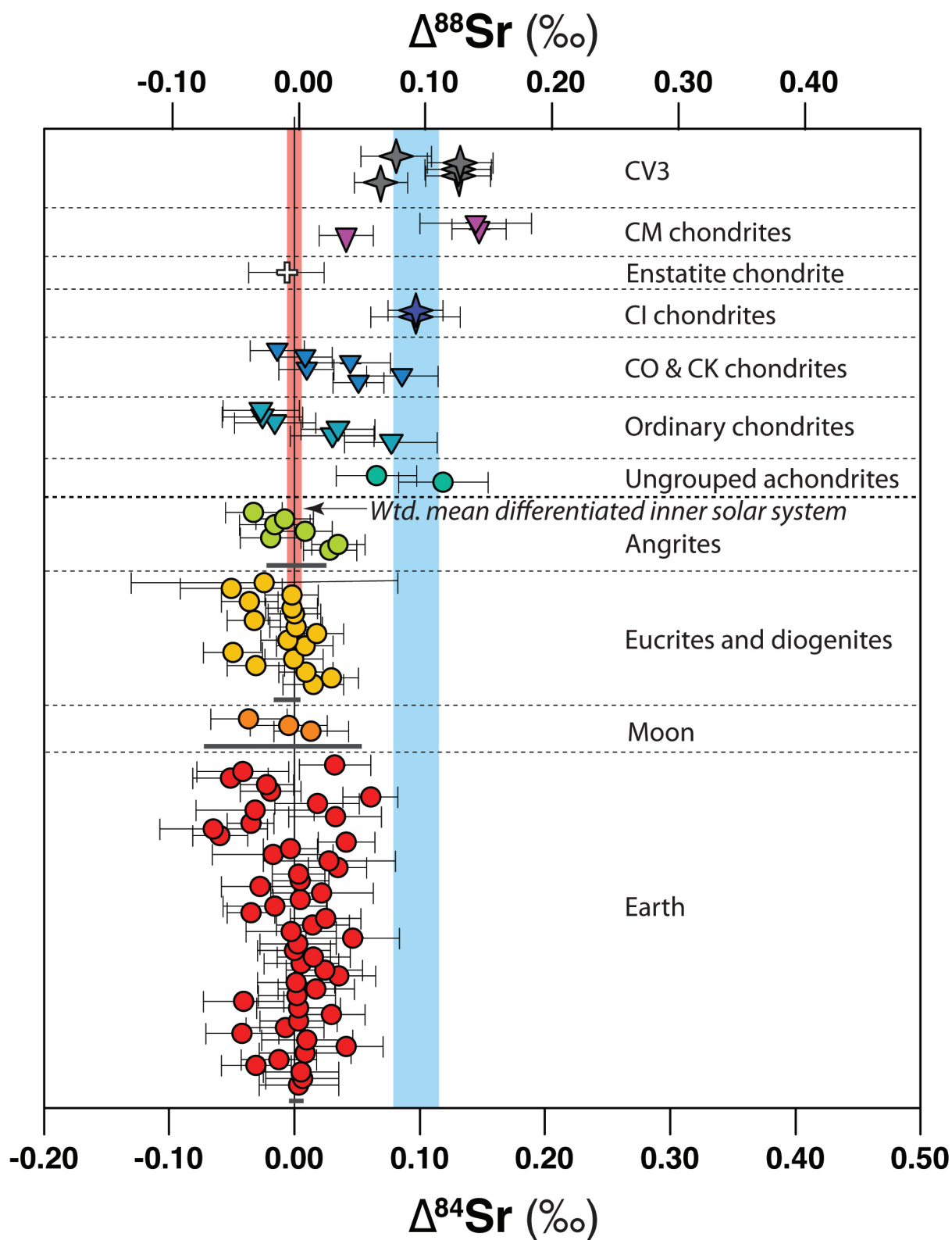
Figure 2 Plot of $\Delta^{84}Sr$ and $\Delta^{88}Sr$ for all samples (see Supplementary Information Table S-1 for data values). Uncertainties are 2 s.d., fully propagated (see Supplementary Information). Weighted mean values (±2 s.d.) for terrestrial, lunar, eucrite, diogenite and angrite samples are shown as horizontal grey bars for each of these data sets. The vertical pink bar extending through the ungrouped achondrite, ordinary chondrite and carbonaceous chondrite data is a weighted mean value (-0.0018 ± 0.0060, MSWD = 4.1) for the inner solar system derived from the terrestrial, lunar, eucrite, diogenite and angrite samples, and corresponds to the 'terrestrial' MDFL in Figure 1. The blue vertical line represents the weighted mean (±2 s.d) for the (largely undifferentiated) samples used to define the 'offset' MDFL (see text for details).

^{84}Sr or ^{88}Sr anomalies?: testing for p- versus r-process anomalies in Sr. As an inescapable consequence of the number of isotopes available, there are two contrasting (but not mutually exclusive) possibilities for the origins of the non-mass-dependent behaviour in Sr: anomalies in *p*-process ^{84}Sr (*e.g.,* Moynier *et al.,* 2012) and/or in *r*-(plus *s*-)process ^{88}Sr (*e.g.,* Qin and Carlson, 2016). If the radiogenic contribution to ^{87}Sr can be accurately determined, then three-isotope plots of (^{87}Sr/^{86}Sr)$_i$ *versus* $\delta^{84/86}$Sr and $\delta^{88/86}$Sr should show in their deviations from a single MDFL which of the isotopes is anomalous, since the ^{87}Sr/^{86}Sr ratio generated by double-spike techniques will also reflect mass-dependent fractionation processes (Neymark *et al.,* 2014). The key to resolving the source of the anomalies therefore lies in determining the initial ^{87}Sr/^{86}Sr characteristics of the relevant materials, both without the effects of radiogenic ingrowth and accounting for mass-dependent effects. The data need to be acquired using TIMS double-spike techniques because of the requirement that the $\delta^{84/86}$Sr ratio also needs to be accurately known in order to constrain the mass-dependent fractionation for all the Sr isotope ratios. Additionally, what is required is a suite of materials where the initial ^{87}Rb/^{86}Sr ratio was extremely low through formation from volatile element depleted materials (either during the initial condensation, or crystallisation from a volatile depleted melt), and any Rb present has remained undisturbed by further processing or secondary alteration. In addition, the discrimination between *p*- and *r*-process anomalies could be addressed through consideration of other isotope systems, such as Mo, Ba or Sm (*e.g.,* Brennecka *et al.,* 2013). However, the relevant data must be obtained from an aliquot of the same dissolution as that used for the Sr isotopic analysis to avoid issues with sample heterogeneity.

The two part nature of the early solar system. Our data are consistent with previous proposals for a primary division between the materials represented by almost entirely undifferentiated, carbonaceous meteorites from the outer solar system, *versus* (almost invariably) differentiated, non-carbonaceous materials from the inner solar system (Warren, 2011; Kruijer *et al.,* 2017). This division is shown, for example, in Cr and Ti (*e.g.,* Trinquier *et al.,* 2009) and Mo and W (*e.g.,* Burkhardt *et al.,* 2012) and in our data is represented by our dual, effectively parallel MDFLs (Fig. 1a,b). Note, however, that some differentiated meteorites isotopically group with the other undifferentiated samples (Tables S-1 and S-2, Figure S-1), such as NWA011 (Warren, 2011) and NWA 5400 (Burkhardt *et al.,* 2017). In turn, our enstatite chondrite sample, although undifferentiated, falls along the terrestrial MDFL as do the lighter end members of the ordinary, CO and CM chondrites (Fig. 1a,b). Kruijer *et al.* (2017) in their proposal for a distinct contrast between inner and outer solar system domains for early-formed objects point out that differentiation sufficient to start the processes of metal separation and core formation occurred also in the outer domain. It is thus not surprising that some differentiated meteorites plot in their isotopic characteristics with the typical undifferentiated suite of materials.

The data variations that can be attributed to mass-dependent processes (*i.e.* the elongation of the data along the MDFL: Fig. 1) in turn have important implications for two aspects of early solar system history. First, our data indicate that high temperature processes have produced resolvable mass-dependent fractionation in materials that have gone to form many of the meteorite classes (both differentiated and undifferentiated) as well as within the terrestrial and lunar materials (*c.f.* Simon and DePaolo, 2010). Second, contrasting interpretations (*e.g.,* Papanastassiou and Wasserburg, 1969; Halliday and Porcelli, 2001; Hans *et al.,* 2013) of the disparities in initial ^{87}Sr/^{86}Sr ratios in BABI, Angra dos Reis and Allende should be reconsidered. We suggest that fractionation

processes (both mass-dependent and mass-independent) prior to radiogenic ^{87}Sr ingrowth must be considered as possible contributors to these disparities, rather than them simply reflecting age differences related to the timing of volatile element depletion. Also, if there is any *r*-process anomaly in ^{88}Sr, then the initial ^{87}Sr/^{86}Sr value is subject to the inaccuracy in any internally normalised data that employs a fixed ^{88}Sr/^{86}Sr ratio for IMF corrections.

Adoption of double-spike techniques is thus central to unlocking accurate, precise measurements and modelling of early solar system processes using Sr isotopes. The unique insights given by double-spike data open up new perspectives on the links between early solar system bodies, illuminating the different contributions to Sr isotopic variability from nucleosynthetic and variably coupled mass-dependent fractionation processes.

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Additional Information

Supplementary Information accompanies this letter at www.geochemicalpers-pectivesletters.org/article1733

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