

^{146}Sm – ^{142}Nd systematics measured in enstatite chondrites reveals a heterogeneous distribution of ^{142}Nd in the solar nebula

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The short-lived ^{146}Sm – ^{142}Nd chronometer ($T_{1/2} = 103$ Ma) is used to constrain the early silicate evolution of planetary bodies. The composition of bulk terrestrial planets is then considered to be similar to that of primitive chondrites that represent the building blocks of rocky planets. However for many elements chondrites preserve small isotope differences. In this case it is not always clear to what extent these variations reflect the isotope heterogeneity of the protosolar nebula rather than being produced by the decay of parent isotopes. Here we present Sm–Nd isotopes data measured in a comprehensive suite of enstatite chondrites (EC). The EC preserve $^{142}\text{Nd}/^{144}\text{Nd}$ ratios that range from those of ordinary chondrites to values similar to terrestrial samples. The EC having terrestrial $^{142}\text{Nd}/^{144}\text{Nd}$ ratios are also characterized by small ^{144}Sm excesses, which is a pure p-process nuclide. The correlation between ^{144}Sm and ^{142}Nd for chondrites may indicate a heterogeneous distribution in the solar nebula of p-process matter synthesized in supernovae. However to explain the difference in $^{142}\text{Nd}/^{144}\text{Nd}$ ratios, 20% of the p-process contribution to ^{142}Nd is required, at odds with the value of 4% currently proposed in stellar models. This study highlights the necessity of obtaining high-precision ^{144}Sm measurements to interpret properly measured ^{142}Nd signatures. Another explanation could be that the chondrites sample material formed in different pulses of the lifetime of asymptotic giant branch stars. Then the isotope signature measured in SiC presolar would not represent the unique s-process signature of the material present in the solar nebula during accretion.

nucleosynthetic anomalies | early earth differentiation | early solar system | ^{142}Nd excess

Chondrites are assumed to be the building blocks of rocky planets, and isotope compositions of most primitive samples are considered to be representative of the bulk composition of the terrestrial planets (1). However, for many elements chondrites from different groups (carbonaceous, ordinary, and enstatite chondrites) preserve small isotope differences. In this case it is not always clear to what extent these variations (or anomalies) reflect isotope heterogeneity of the protosolar nebula where these elements were synthesized by different nucleosynthetic processes rather than being produced by the decay of parent isotopes. Such a question is particularly pertinent to the study of extinct radioisotope systems, such as ^{146}Sm – ^{142}Nd (half-life of 103 Ma), because the variation in the daughter isotope is always low and close to the analytical resolution. A difference of 20 parts per million (ppm) has been measured between chondrites and terrestrial samples (2). The ^{142}Nd excess in terrestrial samples suggests that these samples come from the long-term evolution of a superchondritic Sm/Nd reservoir. Alternatively the terrestrial ^{142}Nd excess could be the result of an early differentiation event (2) or the direct signature of the accreted material forming planetary bodies in the Mars–Earth region (3). However small differences in stable Nd isotope ratios have also been mea-

sured in carbonaceous chondrites relative to ordinary chondrites and eucrites, which are also characterized by higher ^{142}Nd deficits relative to terrestrial samples (2, 4, 5). Deviations in ^{144}Sm relative to terrestrial material have been also measured in carbonaceous chondrites suggesting that they are not a good reference for the Sm–Nd composition of the bulk Earth.

Isotopic anomalies reported for stable isotopes reflect the distinct stellar nucleosynthetic contributions to the early solar system. Both Sm and Nd comprise seven isotopes synthesized by different nucleosynthetic processes in different environments: p-process (photodisintegration in supernovae), and/or s-process [slow neutron addition in asymptotic giant branch (AGB) stars], and/or r-process (rapid neutron addition process in supernovae). The determination of the Sm–Nd isotope compositions of chondrites provides a powerful means for assessing the provenance of early solar system material. The similarity between the silicate Earth and enstatite chondrites on the basis of their oxygen isotopic compositions has already been taken as evidence that they may dominate Earth's precursor material (6) whereas volatile-rich material would have accumulated toward the end of terrestrial accretion (7, 8). Despite this, there is little ^{146}Sm – ^{142}Nd data on enstatite chondrites (EC) and the two samples that have been studied so far, Abee and Indarch (EH4) possess $^{142}\text{Nd}/^{144}\text{Nd}$ ratios that differ by 20 ppm (2, 5). Here we present Sm and Nd isotope measurements for a large number of EC, a unique class of meteorites comprising highly reduced mineral assemblages formed under very low oxygen fugacity conditions (9, 10). Under these extremely reducing conditions, most of lithophile elements are concentrated in unusual minerals mainly as sulphides, whereas rare earth elements (REEs) are largely distributed in two different phases, enstatite and oldhamite (CaS) (11, 12).

Thirteen EC belonging to both high Fe, high siderophile (EH) and low Fe, low siderophile (EL) subgroups have been selected for isotope measurements. These samples have been little affected by weathering, which can be easily identified because oldhamite is a highly hydrophilic mineral. Eight of those samples are unequilibrated chondrites (ALHA77295, Kota-Kota, MAC02837, MAC02839, MAC88180, Sahara 97072, Sahara 97096, Sahara 97158) and the others are from petrographic type 4 to 6 (Eagle, Hvittis, Indarch, Khairpur, St. Mark's). For all samples Sm and Nd have been separated from the same meteorite dissolution and isotope measurements have been performed once

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isobaric interferences were reduced to negligible levels using the Thermo Fischer Triton thermal-ionization mass spectrometer. Analytical techniques are presented in more detail in *SI Text* attached to this paper.

Results

The EC analyzed in this study have $^{142}\text{Nd}/^{144}\text{Nd}$ ratios ranging from -18 to $+3$ ppm relative to the mean value obtained for the repeated measurement of the JNdi-1 terrestrial standard analyzed in the same conditions, where $(\mu^{142}\text{Nd} = \{(^{142}\text{Nd}/^{144}\text{Nd})_{\text{sample}} / (^{142}\text{Nd}/^{144}\text{Nd})_{\text{standard}} - 1\} \times 10^6)$ (Fig. 1). The range of $^{142}\text{Nd}/^{144}\text{Nd}$ ratios measured in EC group is higher than the external precision obtained on repeated measurements of both the Nd standard and chondrite samples ($2\sigma = 6$ ppm). For comparison, one ordinary chondrite (Jilin, H5) and one carbonaceous chondrite (Allende, CV3) have been measured during this study. Measured $^{142}\text{Nd}/^{144}\text{Nd}$ ratios are similar to the average $^{142}\text{Nd}/^{144}\text{Nd}$ ratios obtained for these groups of meteorites. Jilin has a $\mu^{142}\text{Nd}$ of -22 ± 5 ppm (OC average = -19 ± 5) and $\mu^{142}\text{Nd}$ of -22 ± 2 and -31 ± 7 have been measured in two different dissolutions of Allende (compared to the CC average = -35 ± 15). When $^{142}\text{Nd}/^{144}\text{Nd}$ ratios are compared to those measured in carbonaceous and ordinary chondrites, enstatite chondrites are the chondrite group the closest to the terrestrial composition (Fig. 1A and B).

Discussion

Variations of $^{142}\text{Nd}/^{144}\text{Nd}$ ratio can be produced by (i) the evolution of reservoirs characterized by different Sm/Nd ratios and formed early in the solar system history, when ^{146}Sm was still alive; (ii) nucleosynthetic heterogeneity in the region of the solar nebula where chondrites were formed; and (iii) secondary processes, such as the neutron fluence effect when material is exposed to galactic cosmic rays.

To evaluate the first of those possibilities, we can consider the $^{147}\text{Sm}/^{144}\text{Nd}$ ratios measured in these samples. We note that EC present a large range of $^{147}\text{Sm}/^{144}\text{Nd}$ and a few samples do not fall on the 4.568 Ga ^{147}Sm - ^{143}Nd isochron defined for chondrites (Fig. 2). However samples that do not lie on that line have $^{143}\text{Nd}/^{144}\text{Nd}$ ratios in the range defined for chondrites, suggesting that the Sm/Nd ratios could have been modified recently, which would have no consequence on the abundance of ^{142}Nd and ^{143}Nd radiogenic isotopes. In comparison to other groups of chondrites, REEs in EC are not only distributed among silicate phases and phosphates but a large part is concentrated in oldhamite, a mineral phase easily weathered. A partial loss of oldhamite would decrease the $^{147}\text{Sm}/^{144}\text{Nd}$ ratio of the bulk sample because this mineral has a superchondritic $^{147}\text{Sm}/^{144}\text{Nd}$ ratio and accounts for at least half of the entire REE budget (11, 12). For example Kota-Kota has the lowest $^{147}\text{Sm}/^{144}\text{Nd}$ ratio (0.167). This sample has not been examined under the microscope by us but it has previously been described as a strongly weathered EC (13). Our observation supports this conclusion because the split we had was the most visibly weathered, both in color and texture, of the samples analyzed here. Moreover Kota-Kota has probably known a more complex history as illustrated by its subchondritic $^{143}\text{Nd}/^{144}\text{Nd}$ ratio ($\epsilon^{143}\text{Nd} = -3.51 \pm 0.04$). When measured $^{147}\text{Sm}/^{144}\text{Nd}$ ratios are compared to $^{147}\text{Sm}/^{144}\text{Nd}$ ratios calculated from $^{143}\text{Nd}/^{144}\text{Nd}$ ratios assuming a simple (single-stage) evolution from initial $^{143}\text{Nd}/^{144}\text{Nd}$ ratios defined for chondrites (1), the variation of the $^{147}\text{Sm}/^{144}\text{Nd}$ ratios is very small, lower than the Sm/Nd range determined for all chondrites (about 4%), except for Kota-Kota (12%). To compare $^{142}\text{Nd}/^{144}\text{Nd}$ ratios obtained in chondrites from different groups, $^{142}\text{Nd}/^{144}\text{Nd}$ ratios have been corrected for a common evolution using a constant $^{147}\text{Sm}/^{144}\text{Nd}$ ratio [0.196, (1)] from 4.568 Ga and an initial solar system $^{146}\text{Sm}/^{144}\text{Sm}$ ratio equal to 0.0085 (14). Calculated

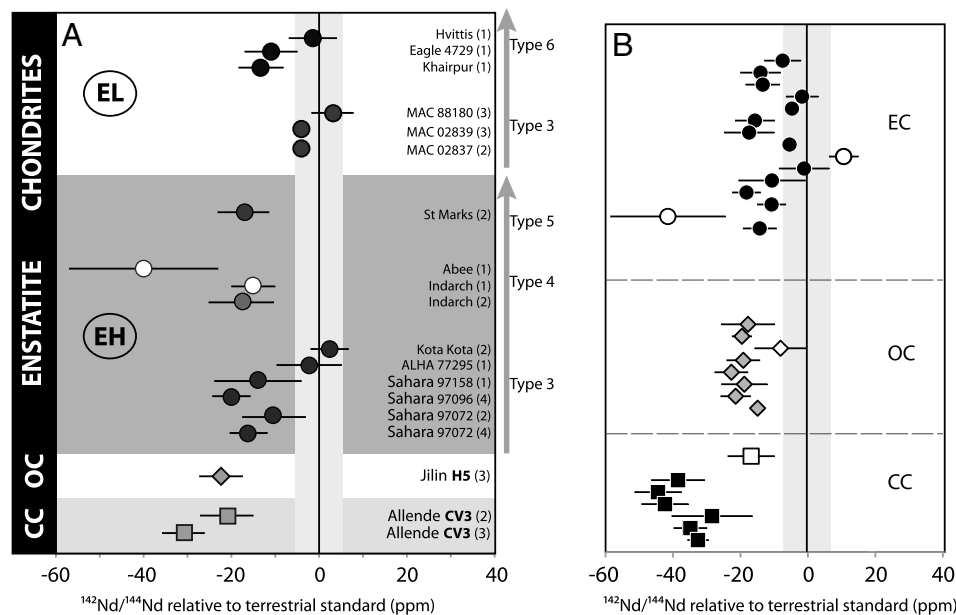


Fig. 1. (A) The $^{142}\text{Nd}/^{144}\text{Nd}$ ratios measured in EC expressed in ppm deviation relative to the mean obtained on the JNdi-1 terrestrial standard measured in the same analytical conditions. Literature values are shown by white symbols (2, 5). The number of measurement is indicated in parenthesis for each sample. When the sample has been measured several times, the error bar represents the two standard deviation of the mean whereas it corresponds to the analytical uncertainty for single measurement (2std error). One ordinary chondrite and one carbonaceous chondrite have been measured in this study. The $^{142}\text{Nd}/^{144}\text{Nd}$ ratios measured for these samples are similar to those reported in the same type of samples (Jilin = -22 ± 5 , OC average = -18 ± 3 ; Allende = -22 ± 2 and -31 ± 7 from two different dissolutions, CC average = -32 ± 3). (B) The $^{142}\text{Nd}/^{144}\text{Nd}$ ratios (ppm deviation) for EC compared to chondrites from different groups (data from 2, 4, 5, 17). Ratios have been corrected to an average chondritic $^{147}\text{Sm}/^{144}\text{Nd} = 0.1960$ (1) and means are shown for samples measured several times. The average values for $^{142}\text{Nd}/^{144}\text{Nd}$ ratios for each chondrite group is: CC = -35 ± 15 ppm ($n = 6$), OC = -19 ± 5 ppm ($n = 7$), EC = -10 ± 12 ($n = 13$). Samples with $^{147}\text{Sm}/^{144}\text{Nd}$ ratios far from the chondritic average of 0.196 have not been considered in the calculation. Moreover Abee has not been considered in the average EC value because the $^{142}\text{Nd}/^{144}\text{Nd}$ ratio reported by Boyet and Carlson (2) has a very large error bar due to the small size of the sample used.

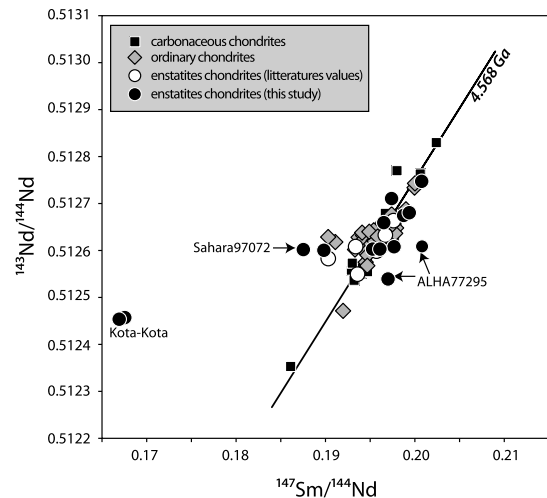


Fig. 2. Samarium and Nd isotope data measured for chondrites from different groups. (A) The $^{143}\text{Nd}/^{144}\text{Nd}$ vs. $^{147}\text{Sm}/^{144}\text{Nd}$ ratios measured of carbonaceous chondrites (squares), ordinary chondrites (diamonds), and enstatite chondrites (circles). Samples measured in this study are shown in blue whereas literature values are in red. The line represents a 4.568 Ga isochron passing through the chondritic average defined by Bouvier et al. (1). Literature data are from (1, 2, 5, 15–18)

$^{142}\text{Nd}/^{144}\text{Nd}$ ratios are very close to measured ratios (Fig. 1B) and the mean obtained for the EC group is -10 ± 12 ppm relative to the JNdi-1 terrestrial standard ratio (Abee and Kota-Kota have not been considered in the calculation). Consequently, variation in the Sm/Nd ratios cannot account for the $^{142}\text{Nd}/^{144}\text{Nd}$ deviation observed between the different groups of chondrites or between the different enstatite chondrites analyzed in this study. The 3 groups of chondrites have different $^{142}\text{Nd}/^{144}\text{Nd}$ ratios with averages of -35 ± 15 ppm (carbonaceous chondrites), -19 ± 5 ppm (ordinary chondrites), and -10 ± 12 ppm (enstatite chondrites).

The sample exposure to galactic cosmic rays can modify the Sm and Nd isotopic composition and then its $^{142}\text{Nd}/^{144}\text{Nd}$ ratio. A long exposure age tends to decrease the $^{142}\text{Nd}/^{144}\text{Nd}$ ratio as observed in lunar samples (19). The secondary neutron capture effect is currently quantified using Sm isotope measurements because ^{149}Sm has the largest thermal neutron capture cross section (e.g., ref. 20). Even if we note a negative correlation between $^{150}\text{Sm}/^{152}\text{Sm}$ and $^{149}\text{Sm}/^{152}\text{Sm}$ ratios (see *SI Text*), ^{149}Sm deficits are lower than -150 ppm, which corresponds to a correction smaller than 1 ppm on the $^{142}\text{Nd}/^{144}\text{Nd}$ ratios [following the approach used by Nyquist et al. (21) or Rankenburg et al. (22)]. This process cannot explain the difference of $^{142}\text{Nd}/^{144}\text{Nd}$ ratios between enstatite chondrites and the 2 other groups of chondrites. As is clearly demonstrated in the ^{149}Sm - ^{150}Sm isotope diagram (*SI Text*), several samples do not plot on the correlation line and the observed scatter could reflect isotope heterogeneities in the solar nebula when chondrites were formed.

We have performed Nd and Sm isotope measurements on the same sample dissolution to evaluate the influence of isotope heterogeneity at the bulk sample scale in EC. Evidence for small-scale Sm isotopic heterogeneity has been observed in carbonaceous chondrites (4, 5) and the highest Sm isotope deviation has been reported for ^{144}Sm , which is a pure p-process nuclide, with deficits ranging from -50 to -120 ppm relative to the terrestrial ^{144}Sm abundance. Samarium isotope ratios have been measured in all EC samples but for only five of them have $^{144}\text{Sm}/^{152}\text{Sm}$ ratios been measured with very high precision (*SI Text*). Two samples, MAC88180 and Hvittis, have positive $\mu^{144}\text{Sm}$ values, whereas other samples are close to the value measured in ordinary chondrites, which is similar to the terrestrial composition

(Fig. 3 A and B). However, the ^{144}Sm variations do not reflect only p-process excess/deficit but can be artificially created by the normalization scheme considered (ratios and mass bias correction). Using the $^{144}\text{Sm}/^{152}\text{Sm}$ ratio and a mass bias correction to $^{147}\text{Sm}/^{152}\text{Sm}$, s-, and/or r-process excesses would produce small deficits in ^{144}Sm . These two processes can be distinguished by also examining the ^{148}Sm and ^{150}Sm abundances because s-process excess must be accompanied by excesses of a similar size for ^{148}Sm and ^{150}Sm whereas r-process excess creates deficits in these both Sm isotopes. Because ^{150}Sm is produced by ^{149}Sm neutron capture and does not reflect the initial isotope composition, the ^{144}Sm is shown relative to the ^{148}Sm abundance in Fig. 3A. There is no correlation between $\mu^{144}\text{Sm}$ and $\mu^{148}\text{Sm}$ for the EC even if several samples have values that lie outside the terrestrial value considering the analytical uncertainties. The absence of any correlation between ^{144}Sm and ^{148}Sm suggests

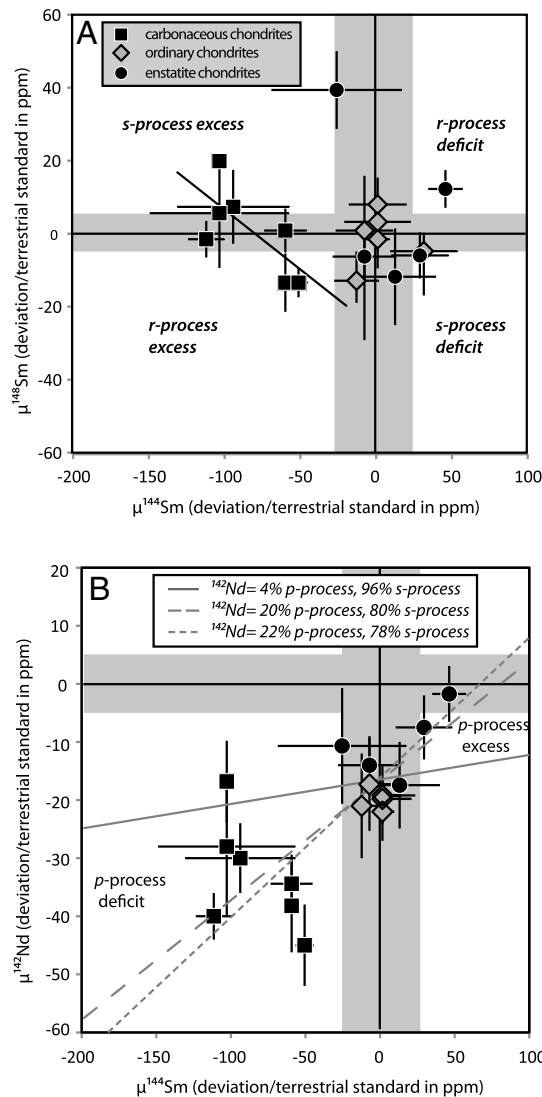


Fig. 3. (A) The $\mu^{144}\text{Sm}$ vs. $\mu^{148}\text{Sm}$. This notation represents the deviation of the Sm isotopic composition measured in meteorites relative to the isotope ratio measured in the terrestrial standard, in part per million (ppm). Data obtained in this study and those from the literature are shown (2, 4, 5, 22). Samarium isotope signatures (normalized to ^{152}Sm) calculated for s- and r- process excess/deficit are indicated. (B) The $\mu^{144}\text{Sm}$ vs. $\mu^{142}\text{Nd}$. Isotopic compositions of meteorite groups lie along the line expected for mixing with p-process when the contribution of p-process is estimated to 20% of the total ^{142}Nd . The ^{144}Sm is a pure p-process isotope.

that s- and r-process deficit/excess is not the cause of the ^{144}Sm variation in this chondrite group. Moreover the same $\mu^{144}\text{Sm}$ values are calculated when Sm isotope ratios are normalized to $^{147}\text{Sm}/^{152}\text{Sm}$ (both isotopes are formed by a mixing of s- and r-processes) or $^{147}\text{Sm}/^{154}\text{Sm}$ (^{154}Sm is a pure r- process nuclide) suggesting that the p-process nuclides were heterogeneously distributed in the solar nebula. Literature data obtained for carbonaceous and ordinary chondrites are also shown on Fig. 3A (4, 5). Ordinary chondrites possess Sm isotope compositions similar to the terrestrial value whereas carbonaceous chondrites have resolvable deficits in ^{144}Sm . The $\mu^{144}\text{Sm}-\mu^{148}\text{Sm}$ correlation line formed by carbonaceous chondrites, shows the presence in variable proportion of an anomalous nucleosynthetic component enriched in s-process. Carlson et al. (5) explained the resolved excesses in $^{148}\text{Nd}/^{144}\text{Nd}$ and $^{150}\text{Nd}/^{144}\text{Nd}$ measured in a few carbonaceous chondrites by an excess of the s-process component. Using the isotopic composition of presolar silicon carbide (SiC) grains as representative of a pure s-process component (23–25), they determined that a positive anomaly in ^{148}Nd would create a similar size deficit in ^{142}Nd . On this diagram, we note that the $\mu^{144}\text{Sm}-\mu^{148}\text{Sm}$ correlation line formed by carbonaceous chondrites does not pass through the $\mu^{148}\text{Sm}$ terrestrial value, suggesting that one part of the deficit in ^{144}Sm could be explained by a p-process deficit (Fig. 2A). For a terrestrial ^{148}Sm abundance, the deficit in ^{144}Sm is ≈ -80 ppm for carbonaceous chondrites. According to the calculation established by Andreasen and Sharma (4), in which the p-process contribution is 4% of ^{142}Nd as suggested in stellar models (26, 27), an 80 ppm deficit in p-process would lower the $^{142}\text{Nd}/^{144}\text{Nd}$ ratio by ± 7 ppm that is not sufficient to reconcile the ^{142}Nd isotope composition of carbonaceous chondrites with that of ordinary chondrites. In this calculation, Andreasen and Sharma (4) consider a $^{146}\text{Sm}/^{144}\text{Sm}$ ratio equal to the production ratio [$P^{146}\text{Sm}/^{144}\text{Sm} = 0.7$ to 2.0, (28)] assuming that only the last addition of Sm in the solar nebula is isotopically anomalous. If instead the solar system initial ratio of 0.0085 (14) is considered, the correction is reduced to 3 ppm. The $^{142}\text{Nd}/^{144}\text{Nd}$ ratios are shown relative to the $^{144}\text{Sm}/^{152}\text{Sm}$ ratios in Fig. 3B. Carbonaceous chondrites in this diagram plot far from other chondrites with both negative $\mu^{142}\text{Nd}$ and $\mu^{144}\text{Sm}$ values whereas enstatite chondrites characterized by a terrestrial ^{142}Nd signature have small excesses in ^{144}Sm . The positive correlation observed between the different groups of chondrites suggests a control of the ^{142}Nd signature in chondrite material by a p-process excess/deficit. However the isotope compositions of meteorites fall on a line characterized by a slope different from that calculated for a variable p-process contribution obtained if the p-production of ^{142}Nd is estimated to be 4% of the total ^{142}Nd . Instead, the correlation line fits the slope obtained for a mixture between normal and pure p-process component calculated if the p-process contribution to ^{142}Nd increases is much higher, around 20%. The Sm and Nd data for chondrites from different groups may suggest that isotopes produced by p-process were heterogeneously distributed in the solar nebula. In this case, this study highlights the necessity of obtaining high-precision ^{144}Sm measurements to interpret properly measured ^{142}Nd signatures before the $^{146}\text{Sm}-^{142}\text{Nd}$ short-lived chronometer can be used as a reliable indicator of early silicate differentiation.

The variation of $^{142}\text{Nd}/^{144}\text{Nd}$ ratios measured in chondrites cannot be explained by s-process excess/deficit considering the Nd isotope composition measured in SiC presolar grains (23–25) that is very close to the s-process signature estimated in stellar models (26). The quoted s-result corresponds to the signature obtained for the whole lifetime of the AGB stars. However, they are accumulated in many pulses and some of them, especially the early ones may contribute slightly different abundances. So another explanation could be that chondrites from different

groups sample material formed in different pulses of the lifetime of AGB stars. Then the isotope signature measured in SiC presolar would not represent the unique s-process signature of the material present in the solar nebula during accretion.

We observe that for EC, most of the unequilibrated samples (EH3 and EL3) have $^{142}\text{Nd}/^{144}\text{Nd}$ ratios similar to the terrestrial value (Fig. 1A). The exceptions to this are the three Sahara samples (97072, 97096, and 97158) thought to be paired. Although these samples are type 3, they record a metamorphic event identified by the breakdown of the major K- and Rb-bearing sulphide (djersfisherite) to troilite as identified in Qingzhen and Yamato 6901 that are both EH3 (29, 30). It has been shown that this postaccretionary thermal metamorphism has affected the inventory of presolar silicate grains in EH3 chondrites (30, 31). We can question whether the isotope compositions measured in samples containing a large proportion of these components represent those of the bulk samples or instead can be ascribed to incomplete dissolutions (32, 33). This is particularly true for components carrying significant isotope anomalies, such as SiC presolar grains in which ^{142}Nd excess of about 8,000 ϵ -unit have been measured (23–25). However, in contrast to the observations made on ordinary chondrites, SiC grains have been described not only in unequilibrated EC but also in well equilibrated samples (34). Hvittis is the only equilibrated EC (EL6) with a terrestrial $^{142}\text{Nd}/^{144}\text{Nd}$ isotope composition but this sample possesses coupled $^{144}\text{Sm} - ^{142}\text{Nd}$ excesses. The average $^{142}\text{Nd}/^{144}\text{Nd}$ ratio obtained for EC chondrites from petrographic type 4 to 6, except Hvittis, which is enriched in nuclides formed by p-process, is -14 ± 5 ppm. This ratio is slightly lower but similar within the analytical uncertainties, to the average ratio obtained for ordinary chondrites (-18 ± 5 ppm). Instead unequilibrated samples (except Sahara 97072, 97096, 97158) have an average $^{142}\text{Nd}/^{144}\text{Nd}$ ratio of -3 ± 4 ppm, which is indistinguishable from the terrestrial ratio. Modeling the long-term evolution of the Earth requires assumption on the nature of the Earth's building material. The ^{144}Sm deficit and coupled $^{148}\text{Nd}-^{150}\text{Nd}$ excesses detected in carbonaceous chondrites relative to terrestrial samples suggest that this group of chondrites is not representative of the bulk composition of the Earth. Thus, the Nd isotope composition of ordinary chondrites with a 20 ppm deficit in ^{142}Nd relative to modern mantle has been used to revisit the mantle-crust evolution (35–37) and it has been proposed that early Earth silicate differentiation occurred during the first 75 Ma of solar system history (2, 38). The very small range of $^{142}\text{Nd}/^{144}\text{Nd}$ ratio measured in ordinary chondrites could represent an artifact caused by sampling bias because no primitive meteorite from this group has been measured with sufficient precision for the determination of small deviations in the abundance of stable Sm isotopes.

The EC represents the chondrite group with the closest $^{142}\text{Nd}/^{144}\text{Nd}$ ratio to the terrestrial value and even if small ^{144}Sm excesses have been reported in samples characterized by terrestrial ^{142}Nd signature, the ^{144}Sm deviation relative to terrestrial material is relatively small and close to the analytical precision obtained using the new generation of thermal-ionization mass spectrometers. The participation of enstatite chondrites in Earth's accretion is based on chemical and isotope evidences (39). Enstatite chondrite and terrestrial samples share similar isotope compositions for a number of elements including oxygen (40), nitrogen (6), molybdenum (41), chromium (42, 43), and titanium (44). The ^{142}Nd offset measured between chondrites and terrestrial samples is reduced to -10 ppm if it is assumed that EC have played a major role in Earth accretion. A small difference in ^{142}Nd abundance still exists between Earth and chondrites suggesting that an enriched hidden reservoir formed during the first few tens of Ma of the Earth's history has been preserved from mantle convection since its formation.

Materials and Methods

All enstatite chondrites were crushed by hand in an agate mortar. About 1 g of homogenized powdered samples were dissolved in a HF–HNO₃ in steel-jacketed tetrafluoroethylene (TFE) Teflon lined Parr bombs. Once a clear solution was obtained, a 5% aliquot was taken and spiked with ¹⁴⁹Sm–¹⁵⁰Nd tracer to measure Sm and Nd concentrations by isotope dilution. The full chemical procedure for the extraction and purification of Sm and Nd followed closely techniques described previously (2). The last step consists on one pass through Ln-spec resin in weak HCl acid. Organic residues are then completely removed and the sample is ready to be loaded on Re filament. Total procedural blanks for Sm and Nd were 1.5 and 8.3 pg, respectively. The spiked fractions have been separated using the method developed by Pin and Santos Zalduegui (45). All the isotopic measurements presented in this study were obtained on the Thermo-Fisher Triton thermal ionisation mass spectrometer at Laboratoire Magmas et Volcans. The Nd was measured in static mode by using the 9 faraday cups, as positive metal ions and measured ratios were corrected for instrumental mass fractionation using the exponential law and ¹⁴⁶Nd/¹⁴⁴Nd = 0.7219. Our current mean value for ¹⁴²Nd/¹⁴⁴Nd in the JNdi-1 standard is 1.1418331 ± 0.0000066 (2σ_m). The external reproducibility on repeated standard analyses is always better than 6 ppm for the given campaign. Ce and Sm interferences are monitored on masses 140 and 147,

respectively. The Sm was measured in static mode as Sm⁺ ions using double Re filaments. Possible isobaric interferences from Nd and Gd were monitored by measuring the intensity on ¹⁴⁶Nd and ¹⁵⁶Gd masses. Sm data were corrected for instrumental mass fractionation using the exponential law and ¹⁴⁷Sm/¹⁵²Sm = 0.56081. The remaining analytical details are cited in *SI Text*.

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- Bouvier A, Vervoort JD, Patchett PJ (2008) The Lu–Hf and Sm–Nd isotopic composition of CHUR: Constraints from unequilibrated chondrites and implications for the bulk composition of terrestrial planets. *Earth Planet Sci Lett* 273:48–57.
- Boyett M, Carlson RW (2005) ¹⁴²Nd evidence for early (>4.53 Ga) global differentiation of the silicate earth. *Science* 309:576–581.
- Caro G, Bourdon B, Halliday AN, Quitté G (2008) Super-chondritic Sm/Nd ratios in Mars, the earth, and the moon. *Nature* 452:336–339.
- Andreasen R, Sharma M (2006) Solar nebula heterogeneity in p-process samarium and neodymium isotope. *Science* 314:806–809.
- Carlson RW, Boyett M, Horan MF (2007) Chondrite barium, neodymium, and samarium isotopic heterogeneity and early earth differentiation. *Science* 316:1175–1178.
- Javoy M (1995) The integral enstatite chondrite model of the earth. *Geophys Res Lett* 22:2219–2222.
- Albarède F (2009) Volatile accretion history of the terrestrial planets and dynamic implications. *Nature* 461:1227–1233.
- Schönbächler M, Carlson RW, Horan MF, Hauri EH (2010) Heterogeneous accretion and the moderately volatile element budget of Earth. *Science* 328:884–887.
- Keil K (1968) Mineralogical and chemical relationships among enstatite chondrites. *J Geophys Res* 73:6945–6976.
- Larimer JW (1968) An experimental investigation of oldhamite CaS; and the petrological significance of oldhamites in meteorites. *Geochim Cosmochim Acta* 32:965–982.
- Crozaz G, Lundberg LL (1995) The origin of oldhamite in unequilibrated enstatite chondrites. *Geochim Cosmochim Acta* 59:3817–3831.
- Gannoun A, Boyett M, El Goresy A, Devouard B (2011) REE and actinide microdistribution in Sahara 97072 and ALHA77295 EH3 chondrites: A combined cosmochemical and petrologic investigation. *Geochim Cosmochim Acta* 10.1016/j.gca.2011.03.017.
- Leitch CA, Smith JV (1982) Petrography, mineral chemistry and origin of Type I enstatite chondrites. *Geochim Cosmochim Acta* 46:2083–2097.
- Boyett M, Carlson RW, Horan M (2010) Old Sm–Nd ages for cumulate eucrites and redetermination of the solar system initial ¹⁴⁶Sm/¹⁴⁴Sm ratio. *Earth Planet Sci Lett* 291:172–181.
- Jacobsen SB, Wasserburg GJ (1980) Sm–Nd isotopic evolution of chondrites. *Earth Planet Sci Lett* 50:139–155.
- Jacobsen SB, Wasserburg GJ (1984) Sm–Nd isotopic evolution of chondrites and achondrites, II. *Earth Planet Sci Lett* 67:137–150.
- Prinzhofer A, Papanastassiou DA, Wasserburg GJ (1992) Samarium–neodymium evolution of meteorites. *Geochim Cosmochim Acta* 56:797–815.
- Patchett PJ, Vervoort JD, Söderlund U (2004) Lu–Hf and Sm–Nd isotopic systematics in chondrites and their constraints on the Lu–Hf properties of the earth. *Earth Planet Sci Lett* 222:29–41.
- Boyett M, Carlson RW (2007) Early lunar differentiation and a non magma ocean origin for the lunar crust. *Earth Planet Sci Lett* 262:505–516.
- Lingenfelter RE, Canfield EH, Hampel VE (1972) The lunar neutron flux revisited. *Earth Planet Sci Lett* 16:335–369.
- Nyquist LE, et al. (1995) ¹⁴⁶Sm–¹⁴²Nd formation interval for the lunar mantle material. *Geochim Cosmochim Acta* 59:2817–2837.
- Rankenburg K, Brandon AD, Neal CR (2006) Neodymium isotope evidence for a chondritic composition of the moon. *Science* 312:1369–1372.
- Zinner E, Amari S, Lewis RS (1991) S-process Ba, Nd, and Sm in presolar SiC from the Murchison meteorite. *Astrophys J* 382:L47–L50.
- Hoppe P, Ott U (1997) Mainstream silicon carbide grains from meteorites. *Astrophysical Implications of the Laboratory Study of Presolar Materials, AIP Conference Proceedings*, eds TJ Bernatowicz and E Zinner 402 (American Institute of Physics, New York), pp 27–58.
- Yin Q-Z, Lee CTA, Ott U (2006) Signatures of the s-process in presolar silicon carbide grains: Barium through hafnium. *Astrophys J* 647:676–684.
- Arlandini C, et al. (1999) Neutron capture in low-mass asymptotic giant branch stars: cross sections and abundance signatures. *Astrophys J* 525:886–900.
- Wisshak K, Voss F, Käppeler F, Kazakov L, Reffo G (1998) Stellar neutron capture cross section of the Nd isotopes. *Phys Rev C* 57:391–408.
- Somorjai E, et al. (1998) Experimental cross section of ¹⁴⁴Sm(α, γ)¹⁴⁸Gd and implications for the p-process. *Astron Astrophys* 333:1112–1116.
- El Goresy A, Yabuki H, Ehlers K, Woolum D, Pernicka E (1988) Qingzhen and Yamato-691: A tentative alphabet for the EH chondrites. *Proceedings NIPR Symposium on Antarctic Meteorites*, 1 (National Institute of Polar Research, Tokyo), pp 65–101.
- Lin Y, El Goresy A (2002) A comparative study of opaque phases in Qingzhen (EH3) and MacAlpine Hills 88136 (EL3): Representative of EH and EL parent bodies. *Meteorit Planet Sci* 37:577–599.
- Ebata S, et al. (2006) Presolar silicate grains in enstatite chondrites. *37th Annual Lunar and Planetary Science Conference abstract no.* 1619.
- Becker H, Walker RJ (2003) Efficient mixing of the solar nebula from uniform Mo isotopic composition of meteorites. *Nature* 425:152–155.
- Dauphas N, Davis AM, Marty B, Reisberg L (2004) The cosmic molybdenum–ruthenium isotope correlation. *Earth Planet Sci Lett* 226:465–475.
- Russell SS, Alexander CM, Ott U, Zinner EK, Pillinger CT (1997) SiC from the Indarch (EH4) meteorite. *Meteorit Planet Sci* 32:719–732.
- Boyett M, Carlson RW (2006) A new geochemical model for the Earth's mantle inferred from ¹⁴⁶Sm–¹⁴²Nd systematics. *Earth Planet Sci Lett* 250:254–268.
- Carlson RW, Boyett M (2008) Composition of the earth's interior: The importance of early events. *Philos Trans R Soc A* 366:4077–4103.
- Caro G, Bourdon B (2010) Non-chondritic Sm/Nd ratio in the terrestrial planets: Consequences for the geochemical evolution of the mantle–crust system. *Geochim Cosmochim Acta* 74:3333–3349.
- Moynier F, et al. (2010) Coupled ¹⁸²W–¹⁴²Nd constraint for early Earth differentiation. *Proc Natl Acad Sci USA* 107:10810–10814.
- Javoy M, et al. (2010) The chemical composition of the Earth: Enstatite chondrite models. *Earth Planet Sci Lett* 293:259–268.
- Clayton RN, Mayeda TK (1984) Oxygen isotope composition of enstatite chondrites and aubrites. *J Geophys Res* 89:245–249.
- Dauphas N, Marty B, Reisberg L (2002) Inference on terrestrial genesis from molybdenum isotope systematics. *Geophys Res Lett* 29 10.1029/2001GL014237.
- Shukolyukov A, Lugmair GW (2004) Manganese–chromium isotope systematics of enstatite meteorites. *Geochim Cosmochim Acta* 68:2875–2888.
- Trinquier A, Bircck JL, Allègre CJ (2007) Widespread ⁵⁴Cr heterogeneity in the inner solar system. *Astrophys J* 655:1179–1185.
- Trinquier A, et al. (2009) Origin of nucleosynthetic isotope heterogeneity in the solar protoplanetary disk. *Science* 324:374–376.
- Pin C, Santos Zalduegui JF (1997) Sequential separation of light rare-earth elements, thorium and uranium by miniaturized extraction chromatography: Application to isotopic analyses of silicate rocks. *Anal Chim Acta* 339:79–89.