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Ultra-high-precision Nd-isotope measurements of geological materials by MC-ICPMS

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Abstract

We report novel techniques allowing the measurement of Nd-isotope ratios with unprecedented accuracy and precision by multi-collector inductively coupled plasma mass spectrometry. Using the new protocol, we have measured the Nd-isotopic composition of rock and synthetic Nd standards as well as that of the Allende carbonaceous chondrite. Analyses of BCR-2, BHVO-2 and GSP-2 rock standards yield mass-independent compositions identical to the JNdi-1 Nd-reference standard, with an external reproducibility of 2.4, 1.6, 1.6 and 3.5 ppm respectively, on $\mu^{142}\text{Nd}$, $\mu^{145}\text{Nd}$, $\mu^{146}\text{Nd}$ and $\mu^{150}\text{Nd}$ (μ representing the ppm-deviation of the ratios from JNdi-1) using $^{148}\text{Nd}/^{144}\text{Nd}$ for internal normalization. This represents an improvement in precision by a factor of 2, 7 and 9 respectively for $\mu^{142}\text{Nd}$, $\mu^{145}\text{Nd}$ and $\mu^{150}\text{Nd}$. Near-quantitative recovery from purification chemistry and sample-standard bracketing allow for the determination of mass-dependent Nd-isotopic composition of samples. Synthetic standards, namely La Jolla and AMES, record mass-dependent variability of up to 1.2 ϵ per atomic mass unit and mass-independent compositions resolvable by up to 3 ppm for $\mu^{142}\text{Nd}$ and 8 ppm for $\mu^{150}\text{Nd}$, relative to JNdi-1. The mass-independent compositions are consistent with equilibrium mass fractionation during purification. The terrestrial rock standards define a uniform stable $\epsilon^{145}\text{Nd}$ of -0.24 ± 0.19 (2SD) relative to JNdi-1, indistinguishable from the mean Allende $\epsilon^{145}\text{Nd}$ of -0.19 ± 0.09 . We consider this value to represent the mass-dependent Nd-isotope composition of Bulk Silicate Earth (BSE). The modest mass-dependent fractionation of JNdi-1 relative to BSE results in potential effects on mass-independent composition that cannot be resolved within the reproducibility of our analyses when correcting for natural and instrumental mass fractionation by kinetic law, making it a suitable reference standard for analysis of unknowns. Analysis of Allende (CV3) carbonaceous chondrite returns an average $\mu^{142}\text{Nd}$ deficit of -30.1 ± 3.7 ppm in agreement with previous studies. The apparent deficit is, however, lowered to -23.8 ± 4.0 ppm while normalizing to $^{148}\text{Nd}/^{144}\text{Nd}$ instead of $^{146}\text{Nd}/^{144}\text{Nd}$. We interpret this as the effect of a possible nucleosynthetic anomaly of -6.3 ± 0.5 ppm in $\mu^{146}\text{Nd}$. As ^{142}Nd and ^{146}Nd are both s-process-dominated nuclides, this hints at the possibility that terrestrial $\mu^{142}\text{Nd}$ excess may not reflect ^{146}Sm decay as widely accepted.

1 Introduction

Neodymium (Nd) is a light rare earth element with seven naturally occurring isotopes – ^{142}Nd (27.13%), ^{143}Nd (12.18%), ^{144}Nd (23.8%), ^{145}Nd (8.3%), ^{146}Nd (17.19%), ^{148}Nd (5.76%) and ^{150}Nd (5.64%), out of which the first two are radiogenic and the rest non-radiogenic. The short-lived ^{146}Sm nuclide, with a half-life currently debated to be either 103 Ma^{1,2} or 68 Ma,³ decays to ^{142}Nd whereas ^{147}Sm , a long-lived isotope of Sm, decays to ^{143}Nd with a half-life of 106 Ga.⁴ Samarium and Nd are both refractory, lithophile elements and hence undergo little elemental fractionation by volatility-related processes in the solar nebula. However, there is limited fractionation of Sm from Nd during silicate partial melting or fractional crystallization in planetary bodies, as the latter is slightly more incompatible in silicate lattices than the former. Thus, the residual mantle and the extracted crust develop anomalies in ^{142}Nd relative to the initial bulk reservoir if this fractionation occurs during the effective lifetime of ^{146}Sm , which is the first 300 million years of Solar System history.^{5,6} The ^{143}Nd composition, on the other hand, is controlled by the long-term evolution of silicate reservoirs over the age of the Solar System. This makes the ^{146}Sm - ^{142}Nd decay system a powerful tracer for silicate differentiation history of planetary bodies. Indeed, several Archean provinces on Earth preserve excesses and deficits in the $^{142}\text{Nd}/^{144}\text{Nd}$ ratio of up to ~10–15 ppm (parts in 10^6) relative to modern terrestrial mantle, providing unambiguous evidence for silicate differentiation in the first few hundred million years after Earth's accretion.^{7–12} Importantly, a ~20 ppm excess in the $^{142}\text{Nd}/^{144}\text{Nd}$ ratio of modern terrestrial mantle relative to chondrites, assumed to be the building blocks of terrestrial planets including Earth, has been identified and attributed to a very early global silicate differentiation of the Earth, possibly within the first ~50 Myr of Solar System formation.¹³ If correct, this implies that the primary differentiation of the proto-Earth into an enriched crust and a depleted mantle occurred prior to the giant impact that formed the Moon at about 4400 Myr ago.¹⁴

Radiogenic ingrowth on ^{142}Nd is generally discernible at the sub- ϵ (parts in 10^4) level owing to the low initial ^{146}Sm abundance,^{15,16} calling for high analytical precision on the order of few tens of ppm or less. Thermal Ionization Mass Spectrometry (TIMS) is the benchmark technique for ^{142}Nd measurements owing to its inherent high precision for Nd, with long-term external precision on $^{142}\text{Nd}/^{144}\text{Nd}$ ratio ranging from 2–6 ppm using new-generation TRITON instruments.^{8,9,17,18} Despite the high precision, TIMS studies were later known to suffer inaccuracies from cup bias during static configuration measurements as well as reservoir mixing on the filament, resulting in significant biases beyond the typical reproducibility of the $^{142}\text{Nd}/^{144}\text{Nd}$ ratio.^{19–21} This raises the concern that some of the variability in the existing early Earth ^{142}Nd record, which is well beyond the external reproducibility quoted in most studies, may reflect analytical artefacts. Moreover, a reassessment of the ^{146}Sm - ^{142}Nd systematics of chondritic meteorites has identified variability in $^{142}\text{Nd}/^{144}\text{Nd}$ that is not correlated to the Sm/Nd ratio, suggesting that terrestrial ^{142}Nd composition could carry an inherited signature from heterogeneity in the initial building material.^{22–24} Distinguishing between a radiogenic or nucleosynthetic origin for the difference in ^{142}Nd composition between Earth and chondrites as well as providing an accurate ^{142}Nd record in early Archean rocks requires the ability to measure all

Nd isotopes to much better precision than currently possible by TIMS. For example, the typical uncertainties in the $^{148}\text{Nd}/^{144}\text{Nd}$ and $^{150}\text{Nd}/^{144}\text{Nd}$ ratios are on the order of ~15 and ~30 ppm, which prevents the identification of potential analytical or nucleosynthetic effects. 9,11,23,24

Another important consideration while investigating ppm-level variations in Nd-isotope ratios is adequately correcting for natural mass-dependent fractionation. Nd isotopes, having a mass range of 142 to 150 amu, possess a mass spread of ~5% and, hence, it is possible that the isotope composition of Nd in natural materials is affected by mass fractionation. Significant mass-dependent variations in Nd stable isotopic composition have been reported for high-purity commercial Nd standards.^{25,26} In addition, chromatographic techniques used for sample purification are known to induce mass-dependent fractionation for a number of elements, including Nd.²⁶ In this regard, acquiring high-quality mass-dependent data together with mass-independent data is essential to ensure the accuracy of high-precision Nd-isotope measurements.

Although inherently less sensitive and possessing a much larger instrumental mass bias than TIMS, Multi-Collector Inductively Coupled Plasma Source Mass Spectrometry (MC-ICPMS) is the preferred tool for high-precision isotope ratio measurements of many heavy elements.²⁷ In this paper, we report improved chemical purification and novel mass spectrometry protocols for high-precision analyses of all Nd isotopes by MC-ICPMS. Based on the repeated analyses of reference rock standards and natural geological materials, we show that it is possible to routinely obtain an external reproducibility of 2.4, 2.0, 1.6, 1.6 and 3.5 ppm on the mass-bias-corrected $\mu^{142}\text{Nd}$, $\mu^{143}\text{Nd}$, $\mu^{145}\text{Nd}$, $\mu^{146}\text{Nd}$ and $\mu^{150}\text{Nd}$ using $^{148}\text{Nd}/^{144}\text{Nd} = 0.241578$ (ref. 28) for internal normalization. This represents a significant improvement in external reproducibility relative to state-of-the-art TIMS studies. 8–11,17,24 Moreover, using sample-standard bracketing, the high yields ensured by our purification scheme allow us to simultaneously derive accurate mass-dependent compositions of unknowns, expressed by the $\epsilon^{145}\text{Nd}$ parameter. The external reproducibility on $\epsilon^{145}\text{Nd}$ is 0.20 ϵ -unit, comparable to that obtained using double-spike techniques.²⁶ Finally, we discuss the implications of our new high-precision dataset towards understanding the mass-dependent and mass-independent Nd-isotopic composition of Bulk Silicate Earth (BSE) as well as the origin of the offset between the ^{142}Nd composition of Earth and chondrites.

2 Analytical procedures

2.1 Samples analyzed and digestion

We selected three terrestrial rock standards provided by USGS, namely the Columbia River basalt BCR-2, the Hawaiian basalt BHVO-2 and the Silver Plume granodiorite GSP-2, as well as the Allende CV3 carbonaceous chondrite for Nd-isotope analysis by MC-ICPMS. The selected rock standards have major element compositions that ranged from felsic to mafic, allowing us to evaluate the robustness of the separation chemistry against different sample matrices. We also analyzed a number of synthetic Nd reference materials including the La Jolla and AMES Nd standards as well as commercially available ICP-MS Nd solution (Alfa Aesar Specpure).

For sample digestion and chemical purification, we used high purity acids and $>18.2 \text{ M}\Omega \text{ cm}^{-1}$ H_2O from MilliQ system. Hydrochloric acid and nitric acid were purified by sub-boiling distillation in Teflon stills from analytical grade stock acids. Seastar supplied the concentrated HF used for sample digestion; concentrated HCl and HNO_3 were from in-house distillation. Whole rock powder samples weighing approximately 0.5–1 g, depending on the concentration of Nd, were digested in Savillex beakers using a 4 : 1 mixture of concentrated HF– HNO_3 at 150°C for two days. Once in solution, the samples were evaporated to dryness and redissolved in 7 M HNO_3 at least three times. In case insoluble fluorides were formed, samples were cycled in aqua regia before adding 7 M HNO_3 . The samples were finally dissolved in 6 M HCl to obtain a clear solution. All sample digestions were carefully scrutinized for complete dissolution and lack of residual fluorides prior to chemical purification. To limit the potential effects of incomplete sample digestion and/or sample heterogeneity, we elected to process sub-aliquots of single large digestions for all the samples investigated here. As such, this approach ensures that the estimate of external reproducibility we derive essentially reflects the chemical purification and mass spectrometry protocols described in this work.

2.2 Nd purification

Instrumental mass bias in MC-ICPMS is greatly affected by matrix effects, leading to inaccurate and imprecise isotope measurements when the sample matrix is not efficiently separated prior to analysis. Elimination of any possible isobaric or spectral interference is also a requirement. There are two direct interferences from adjacent rare earths that can potentially affect the accuracy of Nd isotopes, namely Ce and Sm. Accurate measurement of Nd isotope ratios thus require quantitative removal of Ce and Sm from Nd as the former interferes on mass 142 and the latter on masses 144, 148 and 150. Furthermore, the use of plasma source mass spectrometry can result in additional interferences in the form of molecular species such as ^{141}PrH , which would compromise the accuracy of ^{142}Nd isotope data. Purity of Nd on par with the reference standard is hence a prerequisite for precise and accurate isotope measurements by MC-ICPMS. To this end, we have developed an improved chemical separation procedure that provides unsurpassed Nd purity along with quantitative recovery ($>99.5\%$) relative to earlier separation schemes. Separation of Nd from the sample matrix is achieved with a three-step chromatographic separation scheme described below and summarized in Table 1.

The first step involves separation of REE fraction from the major elements on a cation exchange column inspired from Fritz *et al.*²⁹ We used a 2 ml capacity Biorad column loaded with AG50W-X8 (200–400 mesh, H^+ form) cation exchange resin. For samples where more material ($>50 \text{ mg}$ per aliquot) had to be processed owing to low Nd concentrations, 20 ml capacity columns were used to prevent saturating the resin. Following dry down from the initial digestion procedure, samples were dissolved in a 5 ml 0.5 M HNO_3 –0.1 M HF solution and loaded onto the column. The high field strength elements (Al, Ti, Zr, Hf *etc.*) and Fe^{3+} were washed off from the column with 2.5 CV 1 M HF as anionic fluorine complexes. The remaining major matrix elements (alkalis, alkali earths *etc.*) were subsequently washed off with 10 column volume (CV) of 2 M HNO_3 . The REE fraction was finally eluted with 10 CV of 6 M HNO_3 .

Separation of Nd from other rare earth elements can be done on Ln-spec resin, a resin developed based on the selective organophosphorous extractant – di(2-ethylhexyl) phosphoric acid (HDEHP). Sm is quantitatively separated from Nd on Ln-spec when eluted with 0.25 M HCl. However, complete separation of the adjacent light rare earths Ce and Pr from Nd is difficult to achieve due to the very small spread in their distribution coefficients for Ln spec resin at low HCl molarities. Conventional column separations using a 20 cm long Ln-spec column at best do not achieve any appreciable separation between Pr and Nd while Ce would typically tail into the Nd fraction. To achieve quantitative separation of Ce from Nd, we used an oxidative extraction technique using HBrO₃ inspired from Tazoe *et al.*³¹ and Li *et al.*³² which is, in turn, based on the liquid–liquid Ce-extraction technique developed by Rehkamper *et al.*³³ This takes advantage of the variability in oxidation states of Ce relative to other REEs. HBrO₃ oxidizes Ce to its tetravalent state whereas the rest of the REE stay in their trivalent state. The dried-down REE fraction from the cation exchange chemistry was dissolved in 1 ml 0.05 M HNO₃–0.025 M HBrO₃ and loaded onto a 0.4 ml Biorad column filled with Ln-spec resin (Eichrom, 50–100 µm). The column was washed with 0.4 ml of load acid and LREEs, except tetravalent Ce that sticks to the resin, were unloaded with 7 ml 0.2 M HNO₃–0.025 M HBrO₃. We achieved >99% removal of Ce from the remaining REE with this oxidation technique. Note that our tests of the Tazoe *et al.*³¹ protocol using 10 M HNO₃–0.02 M KBrO₃ produced separates containing uncorrectable levels of residual Ce, as well as residual matrix and heavy REEs. Therefore, we adopted the 0.2 M HNO₃–0.025 M HBrO₃ elution, which ensures a light REE separate with low levels of major elements and typical <100 ppm interference level of ¹⁴²Ce that provides an ideal starting point for further automated column processing. HBrO₃ was prepared from a KBrO₃ solution by removing K⁺ ions using cation exchange on AG50W-X8 resin. HBrO₃ decomposes readily to give Br₂ at room temperature and hence was stored refrigerated for up to three months with no apparent decrease in Ce separation efficiency.

Separation of Pr from Nd is challenging owing to their extremely close distribution coefficients for Ln-spec resin. We used the PrepFAST-MC automated column chemistry system supplied by Elemental Scientific to perform elutions on a 80 cm length × 0.24 cm inner diameter column allowing for nearly quantitative separation of Nd from Pr. The Ce-free REE fraction was dissolved in 1 ml of 0.05 M HCl and loaded onto the column. The Ba, La, Pr and any remaining Ce was eluted with 21 ml of 0.2 M HCl at 20 µl min⁻¹. The pure Nd fraction was recovered with 6 ml of 0.2 M HCl at 100 µl min⁻¹. This results in >99% recovery of Nd with >95% separation of Pr.

A final clean-up step aimed at removing any organics and phosphates discharged from resin was also performed for all samples as these impurities were found to compromise the accuracy of the isotope data through enhanced matrix effects during mass spectrometry. The clean-up included passing the separated Nd fraction on 100 µl capacity Biorad columns loaded with AG50W-X8 resin (200–400 mesh, H⁺ form) in 1 M HNO₃, washing off organics with 10 CV of 1 M HNO₃ and unloading pure Nd fraction in 7 M HNO₃. Samples were finally treated in few drops of concentrated HNO₃ to break down any organic residues from the last column. Total procedural blanks from the entire separation chemistry including sample dissolution were <100 pg, and are insignificant considering the amount of processed Nd.

2.3 Nd-isotope measurements by MC-ICPMS

All Nd isotope measurements were made using the *Prometheus* and *Pandora* Thermo Scientific Neptune Plus MC-ICPMS instruments located at the Centre for Star and Planet Formation (Natural History Museum of Denmark, University of Copenhagen). Following Nd separation, samples were dried down, dissolved in 2% HNO₃ and introduced into the plasma source *via* an ESI Apex IR desolvating nebulizer. The typical sample aspiration rate was 45–55 µl min⁻¹. The seven Nd isotopes, ¹⁴²Nd, ¹⁴³Nd, ¹⁴⁴Nd, ¹⁴⁵Nd, ¹⁴⁶Nd, ¹⁴⁸Nd and ¹⁵⁰Nd were collected in static low-resolution mode with Faraday cup detectors connected to amplifiers with 10¹¹ feedback resistors. In addition, to correct for isobaric interferences from Ce and Sm on the ¹⁴²Nd, ¹⁴⁴Nd, ¹⁴⁸Nd and ¹⁵⁰Nd peaks, ¹⁴⁰Ce and ¹⁴⁷Sm were monitored in Faraday cup detectors connected to amplifiers with 10¹² Ω feedback resistors (Fig. 1). To maximize ion transmission and enhance sensitivity, we combined the Thermo Fisher Jet sample cone with the skimmer X-cone. This resulted in a typical sensitivity of ~500 V per ppm Nd under these analytical conditions. Data was acquired using the sample-standard bracketing technique and each sample analysis was interspaced with analyses of the JNdi-1 reference standard. A single analysis consisted of a total of 834 s of baseline measurements obtained on peak (in the same 2% HNO₃ used to dissolve sample and standards) and typically 417–834 s of data acquisition (50–100 cycles with an integration interval of 8.34 s each). Peak centering was performed at the beginning of each standard analysis and a washout time of 60 s was used between sample and baseline measurements. Samples were typically analyzed with a ¹⁴²Nd signal intensity of 35 V and the beam intensities of samples and standards were matched within 5% of each other. Each sample was systematically analyzed 10 times, which corresponds to approximately 12 hours of continuous measurement and a total of about 1 µg Nd consumed per sample.

All data reduction was conducted offline using *iolite*, a data reduction package that runs within the Igor Pro software from Wavemetrics.³⁴ The data reduction scheme used is available from the authors on request. *Iolite*'s smooth spline auto choice was used to interpolate the baseline intensities as also the mass bias with time of reference standards. Smooth auto-spline determines a theoretically optimal degree of smoothing based on the variability throughout an analytical session, which corresponds to 16–24 hours of continuous measurement without adjusting the instrument's tuning parameters. For each analysis, the mean and standard error of the measured ratios were calculated, using a 2 SD threshold to reject outliers. Sample analyses were combined ($n = 10$) to produce an average weighted by the propagated uncertainties of individual analyses.

The stable (*i.e.* mass-dependent) Nd isotope compositions are reported as relative deviations from the JNdi-1 Nd reference standard in the ϵ notation according to the following formula:

$$\epsilon^x\text{Nd} = \left[\frac{(^x\text{Nd}/^{144}\text{Nd})_{\text{sample, measured}}}{(^x\text{Nd}/^{144}\text{Nd})_{\text{JNdi-1, measured}}} - 1 \right] \times 10^4 \quad (1)$$

where $x = 142, 143, 145, 146, 148$ or 150 . In this respect, the $\epsilon^{145}\text{Nd}$ parameter reflects the amount of natural mass-dependent fractionation experienced by a sample relative to the

reference standard per atomic mass unit and is used here to express the stable mass-dependent Nd isotope composition of unknowns. The mass-independent composition reflect deviations of the internally normalized ratios of the sample from that of the JNd-1 Nd standard, both normalized to $^{146}\text{Nd}/^{144}\text{Nd} = 0.7219$ or $^{148}\text{Nd}/^{144}\text{Nd} = 0.241578$ using exponential law to correct for instrumental mass fractionation, and is reported as follows in the μ notation:

$$\mu^x\text{Nd} = \left[\frac{(^x\text{Nd}/^{144}\text{Nd})_{\text{sample, corrected}}}{(^x\text{Nd}/^{144}\text{Nd})_{\text{JNd-1, measured}}} - 1 \right] \times 10^6 \quad (2)$$

This mass-independent component includes the radiogenic ingrowth, effects from nucleosynthetic heterogeneity and/or any physical non-mass-dependent fractionation affecting the sample.

3 Results and discussion

3.1 Instrument stability and internal precision

Stability of measurement conditions is an important factor controlling the precision, reproducibility and accuracy of isotope ratios when measured by MC-ICPMS. Short-term variations in signal intensity or instrument conditions invalidate the assumption that mass bias varies smoothly and hence can be interpolated between two bracketing standards when the sample-standard bracketing protocol is employed to correct for mass bias drift. Similarly, temporal fluctuations in the nature of mass bias that cannot be accounted for when using a single mass-fractionation law for internal normalization may result in residual effects in $\mu^x\text{Nd}$ values compromising the accuracy of mass-independent data. An obvious method to circumvent these potential problems is to stabilize the sample introduction system and plasma ion source as well as optimize run conditions such that signal stability is ensured during the entire course of an analysis. To this end, we tested two sample introduction systems during the course of our study, namely the ESI Apex IR and the Aridus II desolvating nebulizers. Initial testing with Aridus II yielded both raw and internally normalized ratios with an internal precision poorer by a factor of 5 compared to the Apex IR. We speculate that the poorer performance of Aridus is due to larger fluctuations in aerosol properties and pressures causing more severe ionization and plasma fluctuations that cannot be corrected by exponential mass fractionation law. Hence, the ESI Apex IR desolvating nebulizer sample introduction system with an attached Actively Cooled Membrane (ACM) module was used for the Nd isotope measurements reported here. The Apex IR yielded a typical sensitivity of ~500 V per ppm Nd at an uptake rate of 45–55 $\mu\text{l min}^{-1}$ and optimal tune settings. The temperatures of the cooler (multi pass condenser) and heater (cyclonic spray chamber) were set at 2 °C and 100 °C, respectively, and N_2 was used as the additive gas. The tune settings, mainly gas flow rates and zoom optics, were carefully optimized before each analytical session to give maximum sensitivity and signal stability. Absolute drift in the Nd ion intensity over a typical analytical session corresponding to 12–18 hours of continuous measurement was 20% or smaller. The internal precision (2SE) on $\mu^{142}\text{Nd}$, $\mu^{143}\text{Nd}$, $\mu^{145}\text{Nd}$, $\mu^{148}\text{Nd}$ and $\mu^{150}\text{Nd}$ for a single 10×8.34 s measurement was

typically 3, 3, 4, 4 and 5 ppm respectively when normalized to $^{146}\text{Nd}/^{144}\text{Nd}$. Using the $^{148}\text{Nd}/^{144}\text{Nd}$ ratio for normalization returns, on average, slightly better internal precisions of 2.5, 3, 4, 2 and 4.5 ppm for $\mu^{142}\text{Nd}$, $\mu^{143}\text{Nd}$, $\mu^{145}\text{Nd}$, $\mu^{146}\text{Nd}$ and $\mu^{150}\text{Nd}$ respectively. The high internal precision obtained reflects the stability of our sample introduction system and instrument conditions, as internal (or within-run) precision is a measure of the steadiness of sample introduction into mass spectrometer as well as the stability of ion source, mass analyzer and detectors. The typical external precision, determined as 2σ error of the mean of ten repeat measurements was always better than 3, 2, 2, 2 and 4 ppm for $\mu^{142}\text{Nd}$, $\mu^{143}\text{Nd}$, $\mu^{145}\text{Nd}$, $\mu^{146}\text{Nd}$ and $\mu^{150}\text{Nd}$ using $^{148}\text{Nd}/^{144}\text{Nd}$ indicating excellent instrument stability over the course of an analytical session.

It is possible to provide a theoretical estimate of the internal precision that can be achieved using our approach by considering the errors on ion beam measurement under typical mass spectrometry conditions. Two processes, namely Poisson noise and Johnson–Nyquist noise, limit the internal precision during ion-beam measurements. Poisson noise reflects the counting noise arising from counting discrete particles whereas Johnson–Nyquist noise is the thermal noise associated with the resistors. We calculate the variance on beam measurement as the quadratic sum of Poisson noise and Johnson–Nyquist noise taking both components into account using the following formula:

$$\sigma_{\text{beam}}^2 = \sigma_{\text{Poisson}}^2 + \sigma_{\text{JN}}^2 = \frac{VeR + 4KT_kR}{T_i} \quad (3)$$

where V is the average voltage measured in the collector (volts), e is the electronic charge, R is the collector resistance (ohms), K is the Boltzmann constant, T_k is the temperature (Kelvin) and T_i is the integration time (seconds). The signal intensities at which the data for this study was acquired well exceeded the threshold voltage where Johnson–Nyquist noise remains dominant (~ 100 mV)³⁵ and hence Johnson–Nyquist noise can be neglected. We thus estimate the theoretical precision on $\mu^{142}\text{Nd}$ from combining the Poisson noise on individual isotope beams by a Monte Carlo approach to be 3 ppm when using $^{146}\text{Nd}/^{144}\text{Nd}$ ratio and 2.5 ppm when using $^{148}\text{Nd}/^{144}\text{Nd}$ ratio for internal normalization. Given the typical internal precision on $\mu^{142}\text{Nd}$ of 3 ppm and 2.5 ppm when using $^{146}\text{Nd}/^{144}\text{Nd}$ ratio and $^{146}\text{Nd}/^{144}\text{Nd}$ respectively for normalization, this indicates that counting statistics primarily controls the uncertainty on our measurements. Similar calculations for $\mu^{143}\text{Nd}$, $\mu^{145}\text{Nd}$, $\mu^{146}\text{Nd}$ and $\mu^{150}\text{Nd}$ using both normalization schemes also suggest that counting statistics account for the bulk of our uncertainty.

3.2 Interference corrections

The light rare earth elements Ce and Sm have isobars that directly interfere with Nd isotopes, namely Ce on mass 142 and Sm on masses 144, 148 and 150. Quantitative removal of Ce and Sm by ion exchange separation is thus a prerequisite for accurate Nd isotope data. The ^{142}Ce interference on ^{142}Nd is estimated based on the measured intensity at mass 140 using Ce isotopic abundance ratio ($^{140}\text{Ce}/^{142}\text{Ce} = 0.7947$)³⁶ and normalizing to $^{148}\text{Nd}/^{144}\text{Nd} = 0.241578$ (ref. 28) to correct for mass bias. Similarly, Sm interferences on ^{144}Nd , ^{148}Nd and ^{150}Nd is estimated from the measured intensity at mass 147 using Sm

isotope abundances and internally normalizing to $^{148}\text{Nd}/^{144}\text{Nd}$ for mass-bias correction. The ^{142}Ce and ^{148}Sm levels in the samples processed through our separation protocol were typically about 2–5 and 10–30 ppm, respectively. Since the measured $^{148}\text{Nd}/^{144}\text{Nd}$ ratio is affected by Sm interference prior to interference correction, a convergent iterative approach is required. However, at the level of Sm left in our samples (<50 ppm of ^{148}Sm), the convergence is reached within one step of iteration and the residual effect is calculated to be at sub ppm level for all Nd isotopes and hence well within the reproducibility of our measurements. To test the robustness of our interference correction procedure, we doped JNdi-1 Nd standard separately with Ce and Sm at levels significantly larger than that of our samples after chemical purification and analyzed them against un-doped JNdi-1. Results from the experiments plotted in Fig. 2 demonstrate that our correction is accurate for $\mu^{142}\text{Nd}$ within uncertainty even at the maximum interference levels of ^{142}Ce and ^{148}Sm tested here, namely 60 and 400 ppm respectively. The same holds true for $\mu^{148}\text{Nd}$ and $\mu^{150}\text{Nd}$. Given that the typical interference levels of ^{142}Ce and ^{148}Sm in our samples are lesser by an order of magnitude, we conclude that our high-precision Nd isotope data are not affected by artifacts resulting from inappropriate correction of isobaric interferences from Ce and Sm.

Another potential difficulty when measuring $\mu^{142}\text{Nd}$ by MC-ICPMS is the molecular interference from ^{141}PrH . Hydride production during sample introduction in MC-ICPMS has been shown to generate significant interference for several other elements.^{37,38} We tested the effect of PrH on ^{142}Nd by analyzing a JNdi-1 Nd standard doped with Pr to match the chondritic $^{141}\text{Pr}/^{142}\text{Nd}$ ratio³⁹ against an un-doped JNdi-1 solution. The $\mu^{142}\text{Nd}$ value for the doped standard returned an excess of 9 ± 1.4 ppm suggesting an effect of about 10 ppm on ^{142}Nd from ^{141}PrH . The magnitude of hydride interferences is expected to scale with the interference-to-analyte ratio. Thus, a reduction of the $^{141}\text{Pr}/^{142}\text{Nd}$ ratio by a factor of >4 is necessary to bring the ^{141}PrH effect to within the external reproducibility obtained on $\mu^{142}\text{Nd}$. The high-resolution REE separation using the PrepFAST automated column chemistry system yielded Nd fractions with $^{141}\text{Pr}/^{142}\text{Nd}$ ratios equivalent to 0.1–0.2, reduced by a factor of 5–10 from the initial $^{141}\text{Pr}/^{142}\text{Nd}$ ratio. At this level of residual Pr in the samples, the hydride interference can be safely assumed to be within the uncertainty on $\mu^{142}\text{Nd}$, namely 2.4 ppm. However, $^{141}\text{Pr}/^{142}\text{Nd}$ marginally exceeded 0.2 in a few samples owing to the occasional variability in elution volumes on the PrepFAST column system. To account for this, the bracketing standards were doped to the same level of Pr as in samples to cancel out any hydride effect when calculating $\mu^{142}\text{Nd}$.

3.3 Automated column chemistry: a new tool for chromatographic separations

During MC-ICPMS analysis, where spectral and isobaric interferences as well as matrix effects can severely impact the accuracy and precision of the data, achieving very high sample purity is of paramount importance. As indicated by doping experiments, eliminating the spectral interference on ^{142}Nd in the form of ^{141}PrH is important for accurate high-precision ^{142}Nd data. Being adjacent rare-earth elements with similar partitioning characteristics, separation of Pr from Nd is extremely difficult. Published elution schemes on Ln-resin in HCl media do not achieve more than 50% separation between Ce and Nd, whereas Pr remains largely unseparated from Nd.^{40,41} However, separation between two closely eluting peaks on a given column can be improved by increasing the column length,

decreasing the column diameter or by using resin with finer particles. Another critical factor influencing the resolution is the flow rate with which the eluent passes down the column. According to plate theory of chromatography, movement of eluent through a column can be considered as movement across successive equilibration chambers of definite height, called theoretical plates.⁴² A higher number of theoretical plates indicate a higher degree of peak resolution. Plate height, in turn, is a function of factors like column packing and nature and velocity of eluent. For a given column, there is an optimal flow rate at which the peak resolution is maximum as higher flow rates inhibit equilibration between the resin and the eluent across plates to allow ion exchange to take place while lower flow rates promote lateral diffusion within the column and consequent peak broadening. Therefore, a long narrow column filled with fine resin operated at the optimal flow rate could potentially improve the resolution compared to a short stubby gravity-driven column filled with coarse resin.

Traditional chromatography techniques in isotope geochemistry almost always rely on gravity-driven column setups. However, gravity columns impose limitations on the column length and resin particle size that can be used, due to the long elution times that can be difficult to be run manually. This makes the traditional column setup unsuitable for very high-resolution separations such as LREE separation. Highperformance liquid chromatography (HPLC) is an improved form of liquid chromatography that allows pressurized eluents to be passed through the column, thus overcoming the limitations on length and resin mesh size. Ireland *et al.*⁴³ recently explored the use of a Teflon-HPLC system for geochemistry/cosmochemistry applications including separation of individual rare earth elements. Although they achieve separation of most rare earth elements with a 70×0.3 cm column filled with fine Ln resin (25–50 μm) operated at a flow rate of 0.5 ml min^{-1} , they do not manage a separation of more than 60% of Pr from Nd. To maximize the separation between Pr and Nd, we tested different column configurations and elution conditions using the PrepFAST-MC automated low-pressure column chemistry system supplied by Elemental Scientific.⁴⁴ This is a fully automated low-pressure chromatography system with a closed column setup and fluoropolymer low paths that allow pre-mixed solutions to be passed through the column at precise flow rates using a syringe pump and collect discrete eluent fractions. It allows column cleaning, conditioning, sample loading, matrix washes and eluent collection to be done at user-defined volumes and flow rates. Sample/reagents are drawn *via* a multi-valve system into a loop connected to the syringe pumps and are then passed through the column when the syringes contract. Multi-valve system allows the column to be bypassed while loading the loop whereas column is connected into the flow path while dispensing the contents of loop onto the column. An air bubble, which has a volume set in proportion to the flowrate needed, buffers the pressure at the column head and prevents mixing of reagent/sample into the syringe MQ. The loop is flushed with MQ between successive loads to ensure that there is no mixing between reagents. We used custommade columns that consisted of Teflon tubing of desired length and diameter filled with resin and frits inserted on both ends, and attached to the PrepFAST system using fittings that ensured a tight seal. The conventional set up used for light rare earth element (LREE) separation consists of 10–20 cm length $\times$ 4 mm internal diameter columns filled with Ln-spec resin of 50–100 μm where the flow rate under gravity is 10–15

$\mu\text{l min}^{-1}$. Nd is eluted in 0.25 M HCl together with the tail of Ce and almost whole of Pr after washing off La and part of Ce. We conducted a series of experiments with longer, narrower columns at different flow rates and acid molarities to better separate individual LREE. Two columns of dimensions, 55 cm length $\times$ 4 cm i.d. and 85 cm length $\times$ 2.4 cm i.d. were particularly tested at flow rates of 100, 50, 25 and 20 $\mu\text{l min}^{-1}$ with 0.25 M HCl, 0.2 M HCl, 0.25 M HNO_3 and 0.2 M HNO_3 as eluents. The 85 cm column performed a better separation of REE compared to the 55 cm column owing to its greater length and narrower diameter. We used a mixed La–Pr–Nd–Sm ICP solution to calibrate the REE separation. Ce was avoided as the high resolution Ln-spec separation was always performed after Ce removal. We found the separation between Pr and Nd to improve with a reduction in flow rate for any given column and eluent. With respect to different eluents, HCl medium was found to be better at separating individual REE than HNO_3 medium. Reducing the acid strength resulted in far greater elution volumes but also a better separation factor between Pr and Nd peaks. In short, the 85 cm length $\times$ 2.4 cm i.d. column at a flow rate of 20 $\mu\text{l min}^{-1}$ using 0.2 M HCl as eluent provided the best possible separation between Pr and Nd. We used fine-grained Ln-spec resin (25–50 μm) for all experiments. This column set up provided nearly 95% separation of Pr while quantitatively recovering Nd after eluting about 25 ml in total (Fig. 3). The total elution time for LREE per sample is about 24 hours.

3.4 Nd-isotope fractionation during chromatographic separation on Ln-spec resin

Ion-exchange chromatography is known to induce mass-dependent isotopic fractionation for a number of elements.^{45–47} For cation-exchange resin, lower atomic number isotopes have been shown to be preferentially held onto the resin and enriched in the tail fraction.⁴⁸ Our strategy to separate Nd from Pr employs a relatively long column with a capacity of about 4 ml resin (85 cm length $\times$ 2.4 cm i.d.), approximately twice the amount normally used for Nd separations.⁴⁹ As mass fractionation associated with non-quantitative recovery may be enhanced when using longer columns, it is important to assess the effect of a non-quantitative recovery on the accuracy of Nd isotope measurements. A 5 μg AMES Nd standard solution was processed through the long-column Ln-spec chemistry and individual 0.5 ml elution fractions were collected along the Nd elution peak. As this experiment was done prior to the final calibration of Nd purification chemistry, the elution parameters (0.25 M HCl at a flow rate of 100 $\mu\text{l min}^{-1}$) were different from the ones finally used for processing samples. We analyzed the fractions collected over the elution interval of 12–18 ml for its Nd isotopic composition against unprocessed AMES Nd and the results are tabulated in Table 2. The individual fractions were characterized by $\epsilon^{145}\text{Nd}$ values of up to +1.7 in the front and up to –2.3 in the tail, indicating significant isotopic fractionation during column chemistry. Heavier isotopes are enriched in the early fractions and the trend progressively changes to light isotope enrichment in the late fractions. The final tailing fraction beyond 18 ml (comprising 0.5% Nd) was not collected for isotopic analysis and therefore it was not possible to derive the average bulk value by mass balance calculations. Correcting for mass fractionation using the exponential (kinetic) law returns non-zero $\mu^{145}\text{Nd}$ values with deficits of up to –16 ppm in the front fractions and excesses up to +13 ppm in the tail fractions. Using equilibrium law for mass fractionation correction returns

similar $\mu^{145}\text{Nd}$ values up to -17 and $+14$ ppm in the front and tail fractions respectively. Collectively, these results suggest a mass-independent origin for the isotope fractionation observed during column chemistry.

Nuclear field shift (NFS) has been suggested as a possible mechanism for natural mass-independent fractionation in a number of previous studies.^{50–52} Fractionation from nuclear field shift follow a mass-independent pattern having the characteristic of the differences in the mean squared nuclear charge radii ($\langle r^2 \rangle$) between isotopes. The mass-independent effect from nuclear field shift can be calculated using the following equation:

$$\varepsilon_{m_i} = \left[\delta \langle r^2 \rangle_{m_1 m_i} - \frac{m_2(m_i - m_1)}{m_i(m_2 - m_1)} \delta \langle r^2 \rangle_{m_1 m_2} \right] \times a \quad (4)$$

where m_i is the atomic mass of a nuclide indexed with i and a is the scaling factor that represents the overall extent of isotope fractionation. Mean-squared nuclear charge radii values are taken from Angeli.⁵³ The observed isotopic pattern when $\mu^x\text{Nd}$ values are plotted as a function of mass number are reproduced within uncertainty using eqn (4) at an optimized value of ' a ' for each fraction as shown in Fig. 5(a–h). We find that the value of ' a ' that produces the best fit to the observed $\mu^x\text{Nd}$ composition correlates linearly with $\varepsilon^{145}\text{Nd}$ (Fig. 4) as is expected from nuclear field shift theory. The observed pattern is accurately reproduced within analytical uncertainty for all Nd isotopes namely, ^{143}Nd and ^{145}Nd , ^{148}Nd and ^{150}Nd , and for most fractions, when the uncertainty on nuclear charge radii is taken to account. However, the predicted ^{142}Nd is different from that measured for fractions A4, A5 and A10; the reason for this discrepancy is unclear. However, we emphasise that the observed isotopic pattern generally correlates well with that predicted for most fractions, suggesting that nuclear field shift effect accounts well for the mass-independent fractionation induced by the long chromatographic column.

We tested the effects of non-ideal recovery of Nd on the isotopic data by analyzing five aliquots of Ames Nd standard processed through the Nd purification scheme where only 95% recovery was purposefully achieved. The processed aliquots yielded an $\varepsilon^{145}\text{Nd}$ of -0.24 ± 0.09 on average, and marginally resolvable effects of -1.8 ± 1.0 , -2.0 ± 1.1 and -3.7 ± 1.9 ppm in $\mu^{142}\text{Nd}$, $\mu^{143}\text{Nd}$ and $\mu^{150}\text{Nd}$ were found relative to the unprocessed Ames Nd. Although the magnitude of these effects are similar to our external reproducibility, the results point to the importance of ensuring $>99\%$ recovery of Nd for accurate Nd isotope measurements when high-resolution chromatography is employed for Nd purification. Hence, for all the samples analyzed in the study, a yield of $\sim 99.5\%$ was ensured.

3.5 Reproducibility and accuracy of Nd-isotope measurements

The long-term reproducibility and accuracy of our analytical protocol was evaluated by analysing five separately processed aliquots of the terrestrial rock standards BCR-2, BHVO-2 and GSP-2 and the Allende carbonaceous chondrite. The data, summarised in Table 3, was acquired in multiple sessions spanning a period of approximately 6 months. Each of the five aliquots of BCR-2, BHVO-2 and GSP-2 were systematically analysed ten

times. Pooling the data over 10 such sequential analyses for a single aliquot (treated as a single sample) resulted in typical uncertainties (2SE) of 2.0, 1.5, 1.0 and 3.0 ppm for mass-independent $\mu^{142}\text{Nd}$, $\mu^{145}\text{Nd}$, $\mu^{148}\text{Nd}$ and $\mu^{150}\text{Nd}$ on average when normalised to $^{148}\text{Nd}/^{144}\text{Nd} = 0.241578$ and 2.5, 1.5, 2.0 and 3.5 ppm when using $^{146}\text{Nd}/^{144}\text{Nd} = 0.7219$ for normalization, which reflects the internal precision of our approach for one sample. The better precision for all isotopes obtained with the $^{148}\text{Nd}/^{144}\text{Nd}$ normalization scheme compared to the $^{146}\text{Nd}/^{144}\text{Nd}$ normalization is in accordance with counting statistics as well as the greater mass dispersion afforded by the $^{148}\text{Nd}/^{144}\text{Nd}$ normalizing pair. Thus, we infer that the best internal precision and external reproducibility is achieved using the $^{148}\text{Nd}/^{144}\text{Nd}$ normalization scheme for analyses by MC-ICPMS. All replicate aliquots of terrestrial rock standards yield Nd isotope compositions identical to the JNdi-1 reference standard. Pooling all the aliquots of the terrestrial standards returns an external reproducibility (2SD, $n = 15$) of 2.4, 1.6, 1.6 and 3.5 ppm for $\mu^{142}\text{Nd}$, $\mu^{145}\text{Nd}$, $\mu^{146}\text{Nd}$ and $\mu^{150}\text{Nd}$, respectively, for the $^{148}\text{Nd}/^{144}\text{Nd}$ normalization. The $^{146}\text{Nd}/^{144}\text{Nd}$ normalization returns an external reproducibility of 3.0, 1.5, 3.2 and 6.4 ppm for $\mu^{142}\text{Nd}$, $\mu^{145}\text{Nd}$, $\mu^{148}\text{Nd}$ and $\mu^{150}\text{Nd}$, respectively. The five aliquots of the Allende carbonaceous chondrite returns an external reproducibility of 4.0, 3.7, 0.5 and 5.6 ppm for the $\mu^{142}\text{Nd}$, $\mu^{145}\text{Nd}$, $\mu^{146}\text{Nd}$ and $\mu^{150}\text{Nd}$, respectively, using the $^{148}\text{Nd}/^{144}\text{Nd}$ normalization, which is marginally worse than that obtained for the terrestrial rock standards using the same normalization scheme. However, we emphasise that the amount of Nd analyzed for Allende is approximately half of that for the terrestrial standards and, therefore, the marginally poor external reproducibility is consistent with counting statistics.

The external reproducibility we document based on multiple analyses of separately processed aliquots of terrestrial rock standards represents a significant improvement relative to earlier studies using TIMS for all Nd isotope ratios. We note that the external reproducibility of Nd isotope measurements is typically evaluated through repeated analyses of pure Nd metal standards, which yields estimates ranging from 2–5 ppm, 3–30 ppm and 19–40 ppm for the $\mu^{142}\text{Nd}$, $\mu^{145}\text{Nd}$ and $\mu^{150}\text{Nd}$ based on the $^{146}\text{Nd}/^{144}\text{Nd}$ normalization scheme.^{9,11,17,24} The poor reproducibility on $\mu^{145}\text{Nd}$ and $\mu^{150}\text{Nd}$ reflects the fact that ^{145}Nd and ^{150}Nd is measured in static mode whereas ^{142}Nd is measured in multidynamic mode. At face value, this suggests that our approach returns a comparable reproducibility for the $\mu^{142}\text{Nd}$ but significant improvement by a factor of >2 and >5 for the $\mu^{145}\text{Nd}$ and $\mu^{150}\text{Nd}$, respectively. However, reproducibility estimates based on pure metal standards do not take into account potential variability induced by residual sample matrix and/or organics as well as possible contribution from PrH^+ on ^{142}Nd . In addition, potential effects from reservoir mixing on the filament^{19,20,54} or static configuration measurements²¹ can induce inaccuracies at the 10 ppm level on $\mu^{142}\text{Nd}$ value. As such, a thorough evaluation of the external reproducibility must be based on the repeated analysis (>5) of separately processed samples and not pure metal standards. When scrutinising recent datasets,^{11,17,24} we note that estimates of external reproducibility based on a limited number of repeated analyses (<5) of samples yield estimates that are ~8 ppm, ~15 ppm and up to ~33 ppm on the $\mu^{142}\text{Nd}$, $\mu^{145}\text{Nd}$ and $\mu^{150}\text{Nd}$, respectively. However, Li *et al.*³² reports an improved estimate of external reproducibility of the $\mu^{142}\text{Nd}$ value based on repeat analyses of rock standards, corresponding to 4–5 ppm. Thus, we conclude that our technique

represents an improvement at least by a factor of ~ 2 , ~ 7 and ~ 9 for the $\mu^{142}\text{Nd}$, $\mu^{145}\text{Nd}$ and $\mu^{150}\text{Nd}$, respectively, compared to state-of-the-art TIMS measurements.

Repeat analyses of the BCR-2, BHVO-2 and GSP-2 rock standards yield external reproducibilities of better than 2 ppm for the $\mu^{143}\text{Nd}$ values. We compare in Table 5 the $\mu^{143}\text{Nd}$ data obtained here for rock standards and the La Jolla reference solution to that of earlier studies relative to the JNdi-1 standard. For BCR-2, our data are in excellent agreement with previously published values. Our $\mu^{143}\text{Nd}$ values are also in very good agreement with most literature data for BHVO-2 and GSP-2, although Chu *et al.*⁵⁵ and Raczek *et al.*⁵⁶ report marginally less radiogenic compositions for GSP-2 and BHVO-2, respectively. Given the consistency of our data with most studies, we infer that this probably reflect an analytical artifact in the dataset of Chu *et al.*⁵⁵ and Raczek *et al.*⁵⁶ The $\mu^{143}\text{Nd}$ value obtained for La Jolla Nd is identical to that calculated from the reference value of $^{143}\text{Nd}/^{144}\text{Nd} = 0.511858.57$. We note that the difference between the $^{148}\text{Nd}/^{144}\text{Nd}$ - and $^{146}\text{Nd}/^{144}\text{Nd}$ -corrected $\mu^{143}\text{Nd}$ returns a negligible value of 0.5 ± 0.9 ppm for the 15 separately processed aliquots of the BCR-2, BHVO-2 and GSP-2 standards. This provides an additional test of the quality of our data, emphasising the lack of artifacts related to the Sm-interference correction as well as non-ideal mass fractionation during sample purification.

Repeat analyses of Allende carbonaceous chondrite returns an average $\mu^{142}\text{Nd}$, $\mu^{145}\text{Nd}$, $\mu^{146}\text{Nd}$ and $\mu^{150}\text{Nd}$ of -30.1 ± 3.8 , 4.3 ± 2.7 , 12.4 ± 1.0 and 10.3 ± 8.6 ppm, respectively, when normalised to $^{146}\text{Nd}/^{144}\text{Nd}$ (Table 4). The $\mu^{142}\text{Nd}$ data obtained are in excellent agreement with earlier estimates from Gannoun *et al.*²⁴ of -31 ± 7 ppm, Boyet and Carlson¹³ of -30.1 ± 5.9 ppm and Andreassen and Sharma²² of -30 ± 6 ppm, although the reference Nd standard used in the latter two studies was not JNdi-1. The $\mu^{145}\text{Nd}$, $\mu^{148}\text{Nd}$ and $\mu^{150}\text{Nd}$ reported are indistinguishable from the standard owing to their reproducibilities on the order of 10, 15 and 30 ppm, hampering direct comparison with our data.

Coupling the near-ideal recovery of Nd afforded by our technique with the sample-standard bracketing approach by MC-ICPMS allow us to investigate the mass-dependent stable Nd isotope composition of the terrestrial standards analysed here, and expressed by the $\epsilon^{145}\text{Nd}$ parameter. The typical uncertainties of individual measurements are ~ 0.1 ϵ -unit, which is comparable to that obtained by double-spike techniques.²⁶ Repeated analyses of the three terrestrial rock standards show little variability (Fig. 6), defining a uniform $\epsilon^{145}\text{Nd}$ value of -0.24 ± 0.19 relative to JNdi-1. The five replicate analyses of the Allende carbonaceous chondrite return an $\epsilon^{145}\text{Nd}$ value of -0.19 ± 0.09 , which is identical to that defined by the terrestrial standards. This observation suggest that neither high-temperature nebular or igneous processes induce mass-dependent Nd isotope fractionation within the resolution of our analyses. Therefore, the $\epsilon^{145}\text{Nd}$ value of -0.24 ± 0.19 we derive for terrestrial standards may represent the stable Nd isotope composition of the Bulk Silicate Earth (BSE). We infer that accurate mass-dependent stable Nd isotope data with a resolution of ~ 0.2 ϵ -unit per atomic mass unit can be routinely obtained with our technique.

A potential pitfall of high-precision Nd isotope analysis by MC-ICPMS is the production of NdH, which could affect the accuracy of the Nd isotope data. We determined the NdH

production to be approximately 6 ppm under typical operating conditions. However, the highly reducible nature of our $\mu^{143}\text{Nd}$ and $\mu^{145}\text{Nd}$ data, which are the two ratios most sensitive to NdH production, suggest that the NdH production is invariant and well-corrected by the sample-bracketing approach. This is further confirmed by the lack of signal fluctuations in the ^{147}Sm -beam during analysis. Finally, the good agreement of our $\mu^{143}\text{Nd}$ data with published literature values further indicates that the potential effects of the NdH production are negligible.

3.6 Mass-dependent fractionation and accuracy of mass-independent data

The accuracy of high-precision $\mu^{142}\text{Nd}$ data may be affected by the degree and nature of the natural mass-dependent isotope fractionation process experienced by the material under investigation. For example, if a material is isotopically fractionated relative to the reference standards following a law that is different from that used to correct for instrumental mass fractionation, the mass discrimination correction will introduce an artificial bias in the corrected Nd isotope data of the unknown material. This potential limitation has been demonstrated for Mg, Ca and Cr isotopes, typically for commercially purified reference materials.^{65–67} We illustrate this effect in Fig. 7a for a hypothetical sample that has undergone mass-dependent equilibrium fractionation relative to the reference standard and analyzed on an MC-ICPMS, where the instrumental mass fractionation is corrected with exponential law. We find that the apparent excess/deficit in $\mu^{142}\text{Nd}$ resulting from inappropriate mass fractionation correction is 2.8 ppm per ϵ -unit of mass-dependent fractionation per amu as recorded by the $\epsilon^{145}\text{Nd}$ value (Fig. 7b). The corresponding effects in $\mu^{143}\text{Nd}$, $\mu^{145}\text{Nd}$, $\mu^{148}\text{Nd}$ and $\mu^{150}\text{Nd}$ values are 1.1, 0.3, 2.7 and 7.9 ppm, respectively. It is worth emphasising that the potential artifacts affecting the $\mu^{148}\text{Nd}$ and $\mu^{150}\text{Nd}$ values resulting from a 1 ϵ -unit per amu of mass dependant fractionation are marginally outside our external reproducibility, which clearly highlights the potential pitfalls when attempting to resolve ppm level mass-independent anomalies in materials characterised by a fractionated stable Nd-isotope composition. Taking advantage of the accuracy and reproducibility of our stable $\epsilon^{145}\text{Nd}$ data (*ca.* 0.2 ϵ unit), we have investigated this potential effect for a number of commercially available Nd reference materials, namely the La Jolla and Ames Nd reference metals as well as a Specpure Nd ICPMS solution supplied by Alfa Aesar. The results of our experiments are given in Table 6, where we report the Nd isotope composition of the various standard solutions against the JNdi-1 reference standard.

The La Jolla Nd reference standard is characterised by a light stable Nd stable isotope composition relative to JNdi-1 ($\epsilon^{145}\text{Nd} = -1.22 \pm 0.02$), with resolved excesses of 3.3 ± 1.5 and 8.2 ± 2.8 for the $\mu^{142}\text{Nd}$ and $\mu^{150}\text{Nd}$ values and resolved deficits of -2.3 ± 1.6 and -1.3 ± 2.1 for the $\mu^{145}\text{Nd}$ and $\mu^{146}\text{Nd}$ values, respectively. The $\epsilon^{145}\text{Nd} = -1.22 \pm 0.02$ we report for La Jolla is in excellent agreement with that of Wakai and Tanaka²⁶ obtained by double-spike technique. Accepting $\epsilon^{145}\text{Nd} = -1.22 \pm 0.02$ at face value, the reported mass discrimination corrected data are in agreement with that predicted if the natural mass dependant fractionation was dominated by equilibrium processes (Fig. 8). In contrast to La Jolla Nd, the stable Nd isotope composition of the AMES Nd is marginally heavy ($\epsilon^{145}\text{Nd} = 0.76 \pm 0.03$), with corresponding $\mu^{142}\text{Nd}$, $\mu^{145}\text{Nd}$, $\mu^{146}\text{Nd}$ and $\mu^{150}\text{Nd}$ values of -1.9 ± 0.3 , 2.0 ± 0.7 , 1.0 ± 1.8 and -6.3 ± 3.4 respectively. The mass discrimination corrected data are

in agreement with those predicted if the observed natural mass dependant fractionation of $\epsilon^{145}\text{Nd} = 0.76 \pm 0.03$ was dominated by equilibrium processes. Finally, the Specpure Nd ICPMS solution returned an $\epsilon^{145}\text{Nd}$ of 0.30 ± 0.03 , and corresponding mass bias corrected $\mu^{142}\text{Nd}$, $\mu^{145}\text{Nd}$, $\mu^{146}\text{Nd}$ and $\mu^{150}\text{Nd}$ of -2.3 ± 1.1 , 1.4 ± 1.6 , 2.2 ± 1.1 and -3.8 ± 1.9 respectively. Similar to the La Jolla and Ames reference standards, the mass discrimination corrected data for the Specpure solution are also in agreement with that predicted if the observed natural mass dependant fractionation was dominated by equilibrium processes. These results clearly demonstrate the commercial purification of Nd can result in variable amounts of mass-dependent fractionation predominately controlled by equilibrium processes. As such, the use of these materials as a reference Nd standard for analysis of unknown samples will result in the introduction of systematic biases in the $\mu^x\text{Nd}$ mass fractionation corrected data when the exponential mass fractionation law is applied to correct for instrumental mass fractionation. In particular, our experiments demonstrate that previously published $\mu^{142}\text{Nd}$ data referenced against the La Jolla standard may be underestimated by 5 and 3 ppm when using the $^{148}\text{Nd}/^{144}\text{Nd}$ and $^{146}\text{Nd}/^{144}\text{Nd}$, respectively, for internal normalization. In contrast, $\mu^{142}\text{Nd}$ data referenced against AMES Nd will be overestimated by 3 and 2 ppm when respectively using $^{148}\text{Nd}/^{144}\text{Nd}$ and $^{146}\text{Nd}/^{144}\text{Nd}$ for internal normalization, which may be at the limit of the typical external reproducibility of Nd isotope data obtained by TIMS. The replicate analyses of the various natural rock standards as well as the Allende meteorite returns a uniform $\epsilon^{145}\text{Nd}$ value of 0.24 ± 0.19 when referenced against the JNdi-1 standard, indicating that the JNdi-1 standard is only modestly fractionated relative to BSE. Assuming that the mass fractionation was dominated by equilibrium processes, the predicted bias on the corrected $\mu^{142}\text{Nd}$ data will be less than 1 ppm for both normalization schemes and, hence, well within the uncertainty of our measurements. As such, we conclude that the absolute Nd isotope composition of the JNdi-1 reference standard best represents that of BSE and, therefore, is the most appropriate reference material for high precision Nd isotope measurements.

3.7 Nd isotopic composition of Allende carbonaceous chondrite and implications for terrestrial $\mu^{142}\text{Nd}$ composition

One of the important applications of the high-precision Nd-isotope analytical protocol developed in this study is related to understanding the long-standing issue of the terrestrial ^{142}Nd excess relative to chondrites. The significant variability that exists in $^{142}\text{Nd}/^{144}\text{Nd}$ ratios within chondrite groups points to the possibility that a component of the terrestrial excess may be due to nucleosynthetic heterogeneity,²⁴ in contrary to the postulation that it results from an early silicate Earth differentiation.¹³ Resolving the source of ^{142}Nd variability between accessible Earth and chondrites requires a better understanding of the Nd isotopic composition of different chondrite groups, including the potential variations in the stable $^{145}\text{Nd}/^{144}\text{Nd}$, $^{146}\text{Nd}/^{144}\text{Nd}$, $^{148}\text{Nd}/^{144}\text{Nd}$ and $^{150}\text{Nd}/^{144}\text{Nd}$ ratios.

We analysed five aliquots from a single 2.5 g digestion of Allende (CV3) chondrite for its Nd isotopic composition and the results yield a $\mu^{142}\text{Nd}$ on average of -30.1 ± 3.7 ppm when using $^{146}\text{Nd}/^{144}\text{Nd} = 0.7219$ for internal normalization, in agreement with previously published TIMS results (Table 4). The $\mu^{145}\text{Nd}$, $\mu^{148}\text{Nd}$ and $\mu^{150}\text{Nd}$ values are 4.3 ± 4.2 , 12.4

± 1.0 and 10.2 ± 8.7 ppm respectively. However, using $^{148}\text{Nd}/^{144}\text{Nd} = 0.241578$ yield a $\mu^{142}\text{Nd}$ of -23.8 ± 4.0 ppm suggesting a shift in the magnitude of the ^{142}Nd deficits by about 6 ppm depending on the normalization ratio. The $^{148}\text{Nd}/^{144}\text{Nd}$ normalization also results in a $\mu^{146}\text{Nd}$ of -6.3 ± 0.5 ppm, suggesting a deficit in $^{146}\text{Nd}/^{144}\text{Nd}$ ratio accompanying $^{142}\text{Nd}/^{144}\text{Nd}$ deficit. The $\mu^{145}\text{Nd}$ and $\mu^{150}\text{Nd}$ values are now 0.9 ± 3.8 and -9.8 ± 5.6 ppm respectively. Using $^{145}\text{Nd}/^{144}\text{Nd} = 0.3487$ for internal normalization also yields resolvable deficits in both $\mu^{146}\text{Nd}$ and $\mu^{142}\text{Nd}$ consistent with that while using $^{148}\text{Nd}/^{144}\text{Nd}$ although the precision is marginally poorer. These results can be interpreted as the expression of a possible deficit in $^{146}\text{Nd}/^{144}\text{Nd}$ ratio of about -6 ppm relative to terrestrial Nd, being propagated during internal normalization to create the larger $^{142}\text{Nd}/^{144}\text{Nd}$ deficit of -30 ppm. This is possible if there is a correlated deficit in s-process isotopes in the material that formed Allende relative to modern terrestrial mantle as ^{146}Nd is an s-process dominated nuclide (63% s, 27% r) whereas ^{142}Nd is a 96% s-process nuclide. The accompanying ^{150}Nd deficit is an expression of the overestimation of the $^{146}\text{Nd}/^{144}\text{Nd}$ to 0.7219. An s-process heterogeneity in the solar system is already known for other elements like Mo and Zr,^{68–70} and it is apparent that such an s-process heterogeneity could affect the Nd system. Earlier studies have attributed the greater ^{142}Nd deficit in carbonaceous chondrites compared to ordinary chondrites to p-process heterogeneity as evidenced by the ^{144}Sm (pure p-process) deficit in them.^{22,23} However, the observed coupled $^{142}\text{Nd}/^{144}\text{Nd}$ and $^{146}\text{Nd}/^{144}\text{Nd}$ deficits is most easily understood as the expression of s-process heterogeneity. This would imply that the terrestrial ^{142}Nd excess relative to chondrites cannot be solely attributed to ^{146}Sm decay and could arise from a greater incorporation of s-process rich components in its building blocks, in apparent contradiction to previous studies that called for a Sm/Nd fractionation during the lifetime of ^{146}Sm to explain the ^{142}Nd excess on Earth. Moreover, an s-process enrichment in the building blocks of Earth relative to chondrites is also consistent with Zr and Mo isotope measurements.^{68,70}

When studying nucleosynthetic heterogeneity in meteorites, the expression of anomalies is dependent on the choice of the isotope pair used for mass-bias correction. For Nd, there are several isotope pairs to choose for internal normalization and the Nd isotope data is conventionally normalized to $^{146}\text{Nd}/^{144}\text{Nd} = 0.7219$. From the viewpoint of accuracy of mass bias correction, it has been shown that precision and accuracy is optimal when a normalizing ratio that has a similar average mass as the ratio of interest is used.⁶⁴ Given that one is interested in $^{145}\text{Nd}/^{144}\text{Nd}$, $^{146}\text{Nd}/^{144}\text{Nd}$, $^{148}\text{Nd}/^{144}\text{Nd}$ and $^{150}\text{Nd}/^{144}\text{Nd}$ ratios together with $^{142}\text{Nd}/^{144}\text{Nd}$ ratio, while investigating radiogenic and nucleosynthetic effects, it is difficult to identify a normalizing ratio that satisfy this requirement for all of them. It is also important to choose a ratio comprising nuclides of similar nucleosynthetic make up, such that any nucleosynthetic heterogeneity in the normalizing ratio is not propagated into the calculated ratios. Since there is no isotope pair for Nd that satisfy both of the above requirements simultaneously, we emphasise the importance of using multiple normalizing ratios to investigate all potential effects.

4 Conclusions

We developed improved protocols for chemical purification and isotopic analysis by MC-ICPMS that allow for the determination of the Nd isotope composition of silicate materials with unprecedented accuracy and precision. The main conclusions of our study can be summarized as follows:

1. Our improved methods for the chemical purification of Nd by ion-exchange chromatography employing an automated column chemistry system yield highly pure Nd fractions free of Ce and Sm with only 5–10% of residual Pr, while ensuring near ideal recovery (>99%).
2. Repeated analyses of reference rock standards demonstrate that it is possible to routinely measure the Nd-isotopic composition of geological materials with an external reproducibility of 2.4, 2.0, 1.6, 1.6 and 3.5 ppm on $\mu^{142}\text{Nd}$, $\mu^{143}\text{Nd}$, $\mu^{145}\text{Nd}$, $\mu^{146}\text{Nd}$ and $\mu^{150}\text{Nd}$ using $^{148}\text{Nd}/^{144}\text{Nd} = 0.241578$ for internal normalization. This represents an improvement in external reproducibility by a factor of 2, 7 and 9 respectively for $\mu^{142}\text{Nd}$, $\mu^{145}\text{Nd}$ and $\mu^{150}\text{Nd}$ relative to earlier TIMS studies.
3. All terrestrial rock standards returned $\mu^{142}\text{Nd}$, $\mu^{145}\text{Nd}$, $\mu^{146}\text{Nd}$ and $\mu^{150}\text{Nd}$ indistinguishable from JNdi-1 within the resolution of our analyses, indicating that JNdi-1 best represents the mass-independent composition of BSE.
4. Sample-standard bracketing coupled with near-quantitative recovery of Nd allows the determination of mass-dependent isotopic composition of samples. Synthetic Nd standards, namely LaJolla and AMES Nd are characterized by $\epsilon^{145}\text{Nd}$ values of -1.22 ± 0.02 and 0.76 ± 0.03 suggesting significant mass-dependent fractionation during Nd enrichment. Correcting for the natural fractionation experienced by these standards with a kinetic law results in resolvable effects on the $\mu^{142}\text{Nd}$, $\mu^{145}\text{Nd}$ and $\mu^{150}\text{Nd}$ indicating that the natural fractionation experienced by these materials was dominated by equilibrium processes. Thus, the La Jolla and AMES reference standards cannot be used to define the Nd isotope composition of the BSE for $^{142}\text{Nd}/^{144}\text{Nd}$, $^{145}\text{Nd}/^{144}\text{Nd}$, $^{146}\text{Nd}/^{144}\text{Nd}$, $^{148}\text{Nd}/^{144}\text{Nd}$ and $^{150}\text{Nd}/^{144}\text{Nd}$ ratios. These standards are therefore unsuitable as reference materials while studying the Nd isotope composition of extraterrestrial and/or early Earth samples.
5. Analyses of terrestrial rock standards and Allende carbonaceous chondrite yield a uniform $\epsilon^{145}\text{Nd}$ value of -0.24 ± 0.19 (2SD) relative to JNdi-1, suggesting that neither nebular nor igneous processes induce mass-dependent Nd isotope fractionation resolvable at 0.20 ϵ level. The mean $\epsilon^{145}\text{Nd}$ value of -0.24 ± 0.19 we derive for our subset of terrestrial and extraterrestrial samples is interpreted as reflecting an accurate estimate of the stable mass-dependent Nd isotope composition of BSE.

6. The results obtained for Allende carbonaceous chondrite reveal that the magnitude of $\mu^{142}\text{Nd}$ deficit is reduced by about 6 ppm when using $^{148}\text{Nd}/^{144}\text{Nd}$ for normalization instead of $^{146}\text{Nd}/^{144}\text{Nd}$, suggesting the existence of a nucleosynthetic anomaly in ^{146}Nd . This is consistent with the observation that ^{142}Nd and ^{146}Nd are both s-process isotopes and s-process heterogeneity has been demonstrated in Solar System materials for other elements.

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Fig. 1.

The collector set-up used with the Neptune Plus MC-ICPMS. Approximate typical voltage measured and the respective amplifier used are shown for each isotope.

Fig. 2. Analysis of JNdi-1 doped with different concentrations of Ce (A) and Sm (B) demonstrating that interference correction is robust up to 60 and 400 ppm respectively of $^{142}\text{Ce}/^{142}\text{Nd}$ and $^{148}\text{Sm}/^{148}\text{Nd}$. Shown in dotted line is the external reproducibility for $\mu^{142}\text{Nd}$.

Fig. 3.

Elution profile of LREE and Sm on automated Ln-spec column (85 cm length $\times$ 2.4 cm i.d. column) using 0.2 M HCl at a flow rate of $20 \mu\text{l min}^{-1}$ until 21 ml followed by a flow rate of $100 \mu\text{l min}^{-1}$ until 27 ml to complete Nd elution and using 0.75 M HCl at a flow rate of $40 \mu\text{l min}^{-1}$ thereafter until 40 ml as eluent for Sm.

Fig. 4.

Linear correlation between the scaling factor ' a ' and $\epsilon^{145}\text{Nd}$ indicating that the fit obtained by optimizing ' a ' for the mass-independent compositions predicted by nuclear field shift theory to observed compositions is consistent with the magnitude of mass-dependent fractionation recorded by $\epsilon^{145}\text{Nd}$ for each fraction.

Fig. 5.

Mass-independent Nd-isotopic composition measured for fractions A3–A10 collected over the Nd elution interval (open symbols) and the calculated isotope composition using nuclear field shift theory with corresponding values of ' a ' (closed symbols). The pattern is well reproduced within uncertainty for all Nd isotopes except ^{142}Nd for a few fractions.

Fig. 6.
The $\epsilon^{145}\text{Nd}$ values for terrestrial rock standards and Allende carbonaceous chondrite showing little variability in the mass-dependent isotope composition of Solar System materials at the level of 0.20 ϵ external precision.

Fig. 7.

Natural logarithms of $^{142}\text{Nd}/^{144}\text{Nd}$ and $^{145}\text{Nd}/^{144}\text{Nd}$ ratios plotted against each other for a hypothetical sample fractionated by mass-dependent equilibrium fractionation ($\beta = -0.49$) and analysed on a mass spectrometer where instrumental mass bias is defined by kinetic law ($\beta = -0.495$) (A). Correction for mass bias by kinetic law (shown by bold arrow) results in an apparent deviation of the sample ratios from that of the standards (shown by dotted line) different from that of the true deviation of the sample from the standard (shown by dotted line). We plot in (B) the $\mu^{142}\text{Nd}$ as a function of $\epsilon^{145}\text{Nd}$ for samples naturally fractionated

by both equilibrium (closed symbols) and kinetic (open symbols) laws. The apparent excess/deficit in $\mu^{142}\text{Nd}$ resulting from inadequate mass fractionation correction is 2.8 ppm per 100 ppm of mass fractionation recorded by $\epsilon^{145}\text{Nd}$.

Fig. 8.

Plotted are the measured (solid) $\mu^x\text{Nd}$ values for synthetic standards LaJolla Nd and AMES Nd as a function of mass number and the predicted (dotted) $\mu^x\text{Nd}$ values calculated by assuming the standards to be naturally fractionated by the equilibrium law to the degree indicated by $\epsilon^{145}\text{Nd}$ parameter and corrected for mass-bias by kinetic law. Error bars on the predicted composition represent the effects on mass-independent composition corresponding to our external reproducibility of 0.2 e inferred for $\epsilon^{145}\text{Nd}$.

Table 1

Chromatographic scheme for Nd purification

Eluent	Vol. (ml)	Elements eluted
Step 1: REE separation^a		
6 M HCl	20	Cleaning
MQ	6	Conditioning
Load sample in 0.5 M	5	
HNO ₃ –0.1 M HF		
1 M HF	5	Al, Ti <i>etc.</i>
MQ	5	
2 M HNO ₃	20	Mg, Ca <i>etc.</i>
6 M HNO ₃	20	Ba + REE
Step 2: Ce clean-up^b		
6 M HNO ₃	5	Cleaning
MQ	5	Conditioning
Load sample in 0.05 M	1	
NO ₃ –0.025 M HBrO ₃		
0.05 M HNO ₃ –0.025 M HBrO ₃	0.4	Conditioning
0.2 M HNO ₃ –0.025 M HBrO ₃	7	Ba, La, Pr, Nd, Sm
6 M HNO ₃	10	Ce + HREE
Step 3: LREE and Sm clean-up^c		
6 M HCl	30	Cleaning
MQ	20	Conditioning
Load sample in 0.05 M HCl	1	
0.2 M HCl	21	La, Pr
0.2 M HCl	6	Nd
0.75 M HCl	12	Sm
Step 4: final clean-up^d		
6 M HCl	1	Cleaning
MQ	0.6	Conditioning
Load sample in 1 M HNO ₃	0.2	
1 M HNO ₃	1	Leftover matrix and resin
7 M HNO ₃	1	Nd

^aBio-rad column with 2 ml AG 50W-X8 200–400 mesh resin.^bBiorad column with 0.4 ml of Ln-spec 50–100 µm resin.^cPrepFAST-MC column with 3.75 ml of Ln-spec 25–50 µm resin.^dBiorad column with 0.1 ml of BioRad AG50W-X8 200–400 mesh resin.

Table 2

Nd-isotope composition of AMES Nd fractions collected along the Nd elution interval relative to unprocessed AMES Nd. Mass bias corrected using exponential law

Fraction	Volume (ml)	$\epsilon^{145}\text{Nd}$	$\mu^{142}\text{Nd}$	$\mu^{143}\text{Nd}$	$\mu^{145}\text{Nd}$	$\mu^{148}\text{Nd}$	$\mu^{150}\text{Nd}$	<i>N</i>
A3	12–13.5	1.77 ± 0.06	-10.4 ± 6.5	-12.8 ± 5.4	-16.2 ± 5.3	5.2 ± 7.6	72 ± 10	1
A4	13.5–14	1.17 ± 0.06	-23.3 ± 6	-15.5 ± 3.9	-11.2 ± 1.2	8.4 ± 5.2	48.0 ± 15.0	4
A5	14–14.5	0.82 ± 0.04	-8.8 ± 1.6	-8.3 ± 1.3	-6.2 ± 1.1	6.7 ± 2.3	40.1 ± 3.1	5
A6	14.5–15	0.28 ± 0.01	-3.9 ± 4.2	-4.7 ± 2.7	-4.9 ± 1.4	3.2 ± 6.5	19.3 ± 6.7	5
A7	15–15.5	-0.23 ± 0.04	-1.1 ± 2.8	-1.8 ± 1.9	0.3 ± 2.2	-0.2 ± 2.6	1.2 ± 2.9	5
A8	15.5–16	-0.86 ± 0.02	1.7 ± 2.1	0.6 ± 2.2	3 ± 1.7	-2.9 ± 3.1	-23.0 ± 4.9	5
A9	16–16.5	-1.35 ± 0.03	3.5 ± 1.5	10.4 ± 1.5	8.7 ± 4.5	-17.6 ± 2.2	-68.5 ± 7.8	3
A10	16.5–18	-2.31 ± 0.04	11.9 ± 4.4	13.8 ± 3.2	12.7 ± 2.7	-16.8 ± 3.8	-80 ± 14	5

Table 3Analytical results for terrestrial rock standards relative to JNdi-1^a

Sample	$\mu^{142}\text{Nd}$	$\mu^{143}\text{Nd}$	$\mu^{145}\text{Nd}$	$\mu^{146}\text{Nd}$	$\mu^{150}\text{Nd}$	$\epsilon^{145}\text{Nd}$	^{142}Ce (ppm)	^{148}Sm (ppm)	<i>N</i>
BCR-2 (1)	-0.6 ± 2.1	1019.4 ± 2.3	-1.0 ± 1.2	-0.8 ± 1.2	0.2 ± 3.3	-0.09 ± 0.10	2	21	10
BCR-2 (2)	-1.2 ± 3.1	1018.7 ± 3.1	1.9 ± 1.7	0.2 ± 1.7	1.4 ± 2.9	-0.39 ± 0.03	3	32	10
BCR-2 (3)	-2.8 ± 0.8	1018.1 ± 1.7	-0.6 ± 0.8	-0.5 ± 1.2	0.4 ± 1.7	-0.28 ± 0.04	2	19	10
BCR-2 (4)	0.4 ± 1.2	1018.2 ± 0.7	0.4 ± 1.5	0.0 ± 1.4	-4.3 ± 3.9	-0.11 ± 0.06	6	23	7
BCR-2 (5)	-1.4 ± 1.7	1016.3 ± 1.1	-0.9 ± 1.0	0.3 ± 0.8	2.2 ± 1.8	-0.27 ± 0.05	4	52	7
BHVO-2 (1)	-1.5 ± 1.7	1698.6 ± 1.0	0.4 ± 0.9	-0.3 ± 1.2	-4.1 ± 3.7	-0.42 ± 0.06	2	19	10
BHVO-2 (2)	-1.7 ± 1.8	1698.0 ± 1.6	0.3 ± 1.3	1.6 ± 1.0	1.2 ± 4.3	-0.35 ± 0.03	1	18	10
BHVO-2 (3)	-0.7 ± 1.5	1699.0 ± 1.2	0.4 ± 2.0	0.5 ± 0.7	1.5 ± 1.8	-0.30 ± 0.04	4	22	10
BHVO-2 (4)	0.5 ± 1.3	1697.9 ± 1.9	1.1 ± 1.3	0.8 ± 1.4	-1.6 ± 1.2	-0.27 ± 0.03	7	25	8
BHVO-2 (5)	0.1 ± 0.6	1699.6 ± 1.5	1.1 ± 2.4	0.6 ± 1.7	-0.5 ± 2.3	-0.15 ± 0.07	5	25	7
GSP-2 (1)	-1.2 ± 1.3	-1444.7 ± 1.2	-0.3 ± 1.3	-0.4 ± 0.7	-0.7 ± 1.4	-0.20 ± 0.09	4	18	10
GSP-2 (2)	-0.3 ± 2.4	-1443.6 ± 1.6	0.3 ± 1.7	1.0 ± 0.8	0.4 ± 2.4	-0.23 ± 0.11	2	17	10
GSP-2 (3)	1.7 ± 1.1	-1441.8 ± 1.2	0.5 ± 1.1	0.2 ± 0.8	-2.1 ± 1.2	-0.22 ± 0.08	1	17	10
GSP-2 (4)	-2.0 ± 1.1	-1443.9 ± 1.0	-0.3 ± 1.3	0.4 ± 0.6	-2.3 ± 2.5	-0.18 ± 0.07	2	18	10
GSP-2 (5)	1.5 ± 2.7	-1443.6 ± 2.3	0.8 ± 2.0	0.1 ± 1.2	1.8 ± 1.8	-0.16 ± 0.04	2	16	10
<i>Average $\pm$ 2sd</i>	-0.6 ± 2.4		0.3 ± 1.6	0.4 ± 1.6	-0.2 ± 3.5	-0.24 ± 0.19			

^aBCR-2, BHVO-2, GSP-2 and Allende replicate analyses represent single sample digestions divided into five aliquots that were individually processed through our Nd purification protocol. Mass-independent data is normalized to ($^{148}\text{Nd}/^{144}\text{Nd}$) = 0.241578. Typical ^{142}Nd intensity = 35 V.

Table 4

Nd-isotopic composition of Allende carbonaceous chondrite relative to JNdi-1

Sample	$\mu^{142}\text{Nd}^a$	$\mu^{143}\text{Nd}^a$	$\mu^{145}\text{Nd}^a$	$\mu^{148}\text{Nd}^a$	$\mu^{150}\text{Nd}^a$	$\mu^{142}\text{Nd}^b$	$\mu^{145}\text{Nd}^b$	$\mu^{146}\text{Nd}^b$	$\mu^{150}\text{Nd}^b$	$\epsilon^{145}\text{Nd}$
Allende (1)	-32.0 ± 3.1	975.2 ± 3.9	5.0 ± 2.0	12.2 ± 2.3	17.5 ± 4.8	-26.7 ± 3.6	1.3 ± 2.2	-6.2 ± 1.1	-5.4 ± 3.9	-0.22 ± 0.05
Allende (2)	-28.3 ± 4.2	976.7 ± 3.4	6.1 ± 2.2	11.8 ± 3.1	9.0 ± 6.4	-21.3 ± 3.5	2.5 ± 1.7	-5.9 ± 1.6	-12.8 ± 4.2	-0.20 ± 0.04
Allende (3)	-31.5 ± 3.5	978.0 ± 2.8	2.9 ± 2.9	12.9 ± 5.3	9.8 ± 7.7	-24.4 ± 2.1	-0.7 ± 2.3	-6.5 ± 2.7	-12.3 ± 3.3	-0.13 ± 0.04
Allende (4)	-31.2 ± 3.5	975.4 ± 2.8	0.9 ± 1.6	13.1 ± 5.9	10.7 ± 6.5	-24.9 ± 2.5	-1.9 ± 2.7	-6.6 ± 3.0	-10.7 ± 5.7	-0.25 ± 0.04
Allende (5)	-27.4 ± 3.6	977.8 ± 2.6	6.6 ± 2.5	12.2 ± 3.7	3.9 ± 5.6	-21.9 ± 3.5	3.1 ± 2.3	-6.2 ± 1.9	-8.0 ± 4.6	-0.14 ± 0.05
<i>Average $\pm 2sd$</i>	-30.1 ± 3.7	976.6 ± 2.3	4.3 ± 4.2	12.4 ± 1.0	10.2 ± 8.7	-23.8 ± 4.0	0.9 ± 3.8	-6.3 ± 0.5	-9.8 ± 5.6	-0.19 ± 0.09

^aData normalized to $^{146}\text{Nd}/^{144}\text{Nd} = 0.7219$.^bData normalized to $^{148}\text{Nd}/^{144}\text{Nd} = 0.241578$. Typical ^{142}Nd intensity = 14 V.

Table 5The ^{143}Nd composition of reference materials from this study and literature values

Sample	$^{143}\text{Nd}/^{144}\text{Nd}^a$	$\mu^{143}\text{Nd}^a$	$^{143}\text{Nd}/^{144}\text{Nd}^b$	$\mu^{143}\text{Nd}^b$	$\mu^{143}\text{Nd}$ (from literature)
BCR-2(mean)	0.512636	1018.1 ± 2.0	0.512636	1018.1 ± 1.9	1019 ± 25^{58} 1015 ± 23^{32} 986 ± 64^{59} 996 ± 29^{40} 1027 ± 37^{60} 1009 ± 35^{61} 1013 ± 35^{55} 1013 ± 23^{62} 1012 ± 74^{56}
BHVO-2(mean)	0.512985	1698.6 ± 1.3	0.512985	1698.8 ± 2.3	1668 ± 31^{59} 1699 ± 12^{63} 1712 ± 23^{61} 1718 ± 27^{60} 1632 ± 35^{55} 1694 ± 74^{56} 1644 ± 19^{62}
GSP-2(mean)	0.511376	-1443.5 ± 1.9	0.511376	-1443.3 ± 2.2	-1476 ± 6^{63} -1418 ± 23^{55} -1488 ± 74^{56} -1447 ± 6^{62}
LaJolla Nd(mean)	0.511859	-498.6 ± 2.3	0.511859	-499.4 ± 3.2	-502 ± 7^{64}

^aData normalized to $^{146}\text{Nd}/^{144}\text{Nd} = 0.7219$.^bData normalized to $^{148}\text{Nd}/^{144}\text{Nd} = 0.241578$.

Table 6

Nd-isotopic composition of synthetic Nd standards relative to JNdi-1

Sample	$\mu^{142}\text{Nd}$	$\mu^{143}\text{Nd}$	$\mu^{145}\text{Nd}$	$\mu^{146}\text{Nd}$	$\mu^{150}\text{Nd}$	$\epsilon^{145}\text{Nd}$	<i>N</i>
LaJolla Nd (1)	4.1 ± 1.2	-498.5 ± 1.2	-2.1 ± 1.8	-1.1 ± 1.6	9.6 ± 3.7	-1.23 ± 0.07	10
LaJolla Nd (2)	2.3 ± 1.6	-500.0 ± 1.6	-3.4 ± 1.6	-2.6 ± 1.3	7.0 ± 2.4	-1.22 ± 0.04	10
LaJolla Nd (3)	3.5 ± 2.3	-497.2 ± 2.0	-1.5 ± 1.9	-0.1 ± 1.1	7.9 ± 2.4	-1.21 ± 0.09	10
<i>Average $\pm$ 2sd</i>	<i>3.3 ± 1.5</i>	<i>-498.6 ± 2.3</i>	<i>-2.3 ± 1.6</i>	<i>-1.3 ± 2.1</i>	<i>8.2 ± 2.8</i>	<i>-1.22 ± 0.02</i>	
AMES Nd (1)	-1.8 ± 1.9	-284.4 ± 1.8	2.5 ± 1.4	2.1 ± 0.9	-5.5 ± 4.3	0.74 ± 0.14	10
AMES Nd (2)	-1.7 ± 0.6	-276.2 ± 1.7	1.7 ± 1.2	-0.1 ± 1.3	-8.7 ± 2.0	0.76 ± 0.02	10
AMES Nd (3)	-2.1 ± 1.0	-276.6 ± 1.2	1.8 ± 0.5	1.0 ± 1.0	-4.8 ± 2.5	0.78 ± 0.02	10
<i>Average $\pm$ 2sd</i>	<i>-1.9 ± 0.3</i>	<i>-279.1 ± 7.5</i>	<i>2.0 ± 0.7</i>	<i>1.0 ± 1.8</i>	<i>-6.3 ± 3.4</i>	<i>0.76 ± 0.03</i>	
Specpure Nd (1)	-3.0 ± 1.6	564.6 ± 1.0	2.2 ± 1.8	3.0 ± 0.9	-4.0 ± 1.4	0.31 ± 0.02	10
Specpure Nd (2)	-2.3 ± 1.3	566.6 ± 1.9	0.3 ± 2.0	1.8 ± 0.9	-2.5 ± 2.3	0.28 ± 0.03	10
Specpure Nd (3)	-1.7 ± 1.2	565.0 ± 1.4	1.7 ± 1.5	1.9 ± 0.8	-4.8 ± 1.9	0.32 ± 0.03	10
<i>Average $\pm$ 2sd</i>	<i>-2.3 ± 1.1</i>	<i>565.4 ± 1.7</i>	<i>1.4 ± 1.6</i>	<i>2.2 ± 1.1</i>	<i>-3.8 ± 1.9</i>	<i>0.30 ± 0.03</i>	