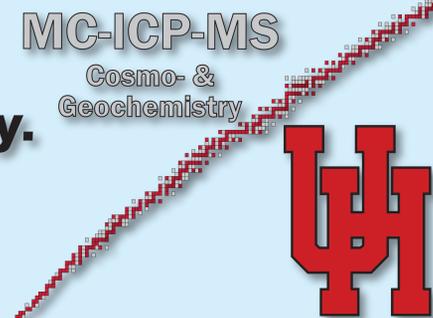


The Absolute Neodymium Isotopic Composition of Standard Materials. Implications for Accurate and Precise ^{142}Nd Measurements and Chronology.



Rasmus Andreasen & Thomas J. Lapen

Department of Earth and Atmospheric Sciences, University of Houston

Introduction

The coupled $^{146,147}\text{Sm}$ - $^{142,143}\text{Nd}$ alpha-decay system is a powerful tool for unraveling early silicate differentiation of planetary bodies. Short-lived ^{146}Sm decays to ^{142}Nd with a recently redetermined half-life of 68 Ma [1], while long-lived ^{147}Sm decays to ^{143}Nd with a half-life of 106 Ga; thus variations in the ^{142}Nd isotopic composition tracks differentiation within the first ~300 Ma of Solar System history, while variations in ^{143}Nd continues to track differentiation. Some of the challenges in utilizing the coupled Sm-Nd system are (i) the low Solar System initial abundance of ^{146}Sm ($^{146}\text{Sm}/^{144}\text{Sm} = 0.0085$) [2] and ^{142}Nd being the most abundant Nd isotope, resulting in very limited variation in the ^{142}Nd composition of usually not more than a few tens of parts per million, and (ii) the fact that ^{142}Nd is the lightest of the Nd isotopes (2-4 amu lighter than ^{144}Nd and ^{146}Nd , traditionally used for instrumental mass bias correction (with $^{146}\text{Nd}/^{144}\text{Nd} = 0.7219$). This makes ^{142}Nd analysis prone to analytical artifacts at the ppm level [3,4]. Luckily, Nd has five stable non-radiogenic isotopes, which makes it possible to detect and correct for the presence of mass-dependent analytical artifacts, if the minor abundance heavy Nd isotopes ^{146}Nd and ^{150}Nd are measured with sufficient precision. In order to do this successfully, however, it is critical to know that samples and standards have the same stable Nd isotopic composition, and that the instrumental mass bias correction is done with an accurate true $^{146}\text{Nd}/^{144}\text{Nd}$ ratio. Stable Nd isotopes have been done by total evaporation by TIMS (e.g. [5]) and by Sm addition for mass bias correction by MC-ICP-MS [6], the former is hampered by poor precision and is unfeasible for many samples, the latter is hampered by adding isobaric Sm interferences to ^{144}Nd , ^{148}Nd , and ^{150}Nd , thus limiting the number of stable non-radiogenic Nd isotopes to two. Here, stable Nd isotopic composition of selected standard materials are analyzed by adding Eu for mass bias correction, thus making it possible to measure all Nd isotopes.

Methods

The stable Nd isotopic compositions of selected standards (Nd isotopic standards La Jolla Nd [7], Caltech nNd- β [8], JNd-i [9], and UH AMES Nd, and USGS rock standards BCR-2 and BHVO-2) were analyzed on the Nu Instruments Nu Plasma II MC-ICP-MS at the University of Houston. The large collector array of the Plasma II (figure 1 - pictured below) makes it possible to simultaneously collect data on masses 140 to 153. This allows the addition of Eu (mass 151 and 153) for mass bias correction in addition to monitoring the isobaric interferences on Nd from Ce and Sm. The isotopic composition of the in-house Eu standard (PlasmaCal Eu) was determined by 6 total evaporation analyses on the Triton Plus TIMS at University of Houston to be $^{153}\text{Eu}/^{151}\text{Eu} = 1.09158 \pm 9$, in agreement with the IUPAC value of 1.0916. Experiments on the Nu Plasma II with the addition of one element to mass bias correct another has shown that there are no measurable differences in the fractionation behavior of Pb & Tl, and Lu & Er, it is here assumed that Nd and Eu do not vary significantly in their fractionation behavior.

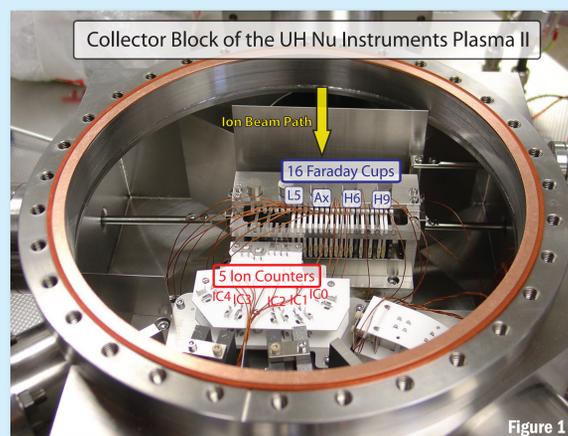


Figure 1

Results

The Eu-normalized Nd isotopic compositions of all the isotopic standards have $^{146}\text{Nd}/^{144}\text{Nd}$ ratios significantly higher than 0.7219, and with some variation among them ranging from La Jolla Nd at 0.7225 to JNd-i and Caltech nNd- β at 0.7227. This is lower than the 0.7241 value suggested by [8] and the total evaporation average of 0.7233 [5], it is much lower than the preferred value of 0.7273 from [10], but very close to the minimum value from [10] of 0.7227. Figure 2 shows the stable Nd isotopic compositions of the four isotopic stand-

ards normalized to ^{146}Nd (in the middle and interference free) and JNd-i. La Jolla Nd is enriched in light Nd relative to JNd-i by a factor about 1 ϵ per amu. This is consistent with the estimate of [6], Caltech nNd- β is enriched in heavy Nd relative to JNd-i at a factor of 0.5 ϵ per amu, AMES Nd is very close in composition to JNd-i, but is slightly heavier at 0.07 ϵ per amu. It is noticeable that La Jolla Nd deviates parabolically from a linear relationship at extreme masses. This implies that La Jolla does not follow the same exponential law fractionation behavior assumed for JNd-i and the other standards, similar effects are seen in TIMS data [5,11-12] both for Nd and for other elements.

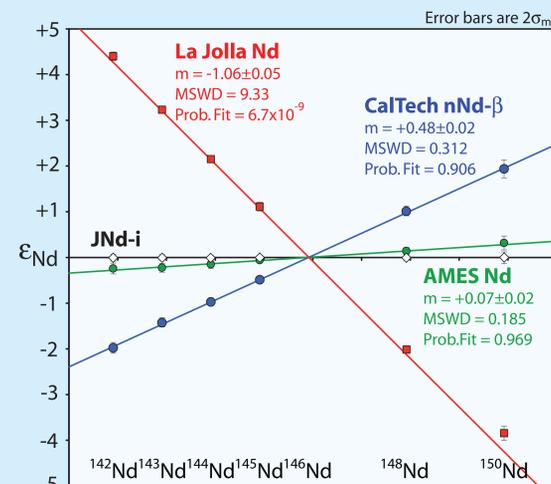


Figure 2: Variations in the isotopic composition of the La Jolla Nd, Caltech nNd- β , and AMES Nd standards relative to JNd-i and normalized to ^{146}Nd . The observed range in mass-dependent Nd isotopic variations is 1.54 ± 0.07 ϵ -units per AMU.

Level of isobaric interferences:

The levels of iso-baric interferences of ^{142}Ce on ^{142}Nd is 2.7 ppm for La Jolla Nd, 1.1 ppm for Caltech nNd- β , 0.8 ppm for AMES Nd and 0.7 ppm for JNd-i; these are comparable with the levels measured by TIMS [13-14]. Pr/Nd levels are 11.3 ppm for La Jolla Nd, 0.8 ppm for Caltech nNd- β , 9.6 ppm for AMES Nd, and 4.5 ppm for JNd-i, suggesting that the Caltech standard is the best suited for NdO TIMS measurements. None of the standards have Sm detectable by Faraday.

Nd isotopic composition of elemental standards:

As variations in radiogenic ^{142}Nd are small, ranging from about 100 parts per million (ppm) in shergottites and nakhlites, to about 35 ppm in chondrites and 10 ppm in terrestrial samples, the radiogenic ^{142}Nd variations are only detectable when internally normalizing the Nd isotopes to a fixed 'true' ratio for one isotope pair, most commonly $^{146}\text{Nd}/^{144}\text{Nd} = 0.7219$. The $^{146}\text{Nd}/^{144}\text{Nd}$ ratios measured here for elemental standards are all significantly higher (8-11 ϵ -units), this suggest that the normalized Nd isotope ratios using $^{146}\text{Nd}/^{144}\text{Nd} = 0.7219$ are not right, though relative differences between samples and standards may be. This is in accord with domain mixing models [3-4,11] that suggest that the absolute values measured for $^{142}\text{Nd}/^{144}\text{Nd}$ are too high. Calculated mass bias corrected Nd ratios are given below in Table 1:

Table 1	$^{142}\text{Nd}/^{144}\text{Nd}$	$^{143}\text{Nd}/^{144}\text{Nd}$	$^{145}\text{Nd}/^{146}\text{Nd}$	$^{146}\text{Nd}/^{144}\text{Nd}$	$^{150}\text{Nd}/^{144}\text{Nd}$
Caltech nNd- β	1.140552	0.511606	0.348593	0.242110	0.237096
JNd-i / AMES Nd	1.140551	0.511606	0.348593	0.242110	0.237095
Caltech nNd- β (0.7219)	1.141833	0.511892	0.348399	0.241578	0.236447

Stable Nd isotopic composition of rock standards:

USGS basalt rock standards BCR-2, a crustally contaminated, Columbia River flood basalt, and BHVO-2, a Hawaiian basalt, were dissolved and Nd was separated using cation and 2-hydroxyisobutyric acid chemistries to get a high-yield >90% Nd cut free of Sm and with <15 ppm Ce interference. These standards were run together with the La Jolla, Caltech, and JNd-i standards. The results are shown in Figure 3; BCR-2 is identical within error to JNd-i in its isotopic composition, whereas BHVO-2 is similar to La Jolla Nd, but seemingly without the deviation in fractionation behavior from JNd-i. Given the high yield of the separation chemistry, it seems unlikely that the difference in isotopic composition between BCR-2 and BHVO-2 is due to fractionation on the column but it cannot be excluded. Organic residues from the breakdown of the 2-hydroxyisobutyric acid appear to have a strong influence on the stability of the mass fractionation as

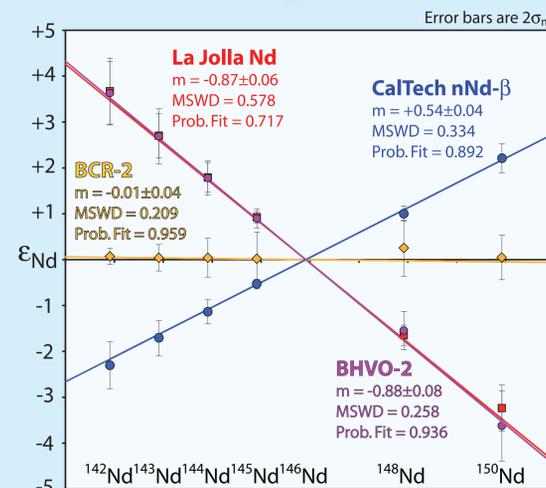


Figure 3: Variations in the isotopic composition of the La Jolla Nd, Caltech nNd- β , and USGS basalt standards BHVO-2 and BCR-2 relative to JNd-i and normalized to ^{146}Nd . The observed range in mass-dependent Nd isotopic variations for the natural standards is 0.89 ± 0.10 ϵ -units per AMU. The presence of residues from the 2-hydroxyisobutyric acid causes instability in instrumental mass fractionation leading to the increased uncertainties compared to those for the data for elemental standards in figure 2.

evident from the relatively large uncertainties for all samples. The influence of the organic acid residue is also observed in TIMS analyses [12] and efforts to remove the residue would result in more accurate TIMS and MC-ICP-MS analyses.

Implications for accurate and precise ^{142}Nd measurements:

An underlying assumption of TIMS data reduction is that any measured sample or standard had a homogenous composition during analysis, if this assumption is violated, it may result in apparent anomalies in the isotopes furthest away from the normalizing isotopes, such as ^{142}Nd . Figure 3 and 4 show the stable isotopic composition of some of the terrestrial samples where negative ^{142}Nd anomalies have been reported. These anomalies are associated with anomalies

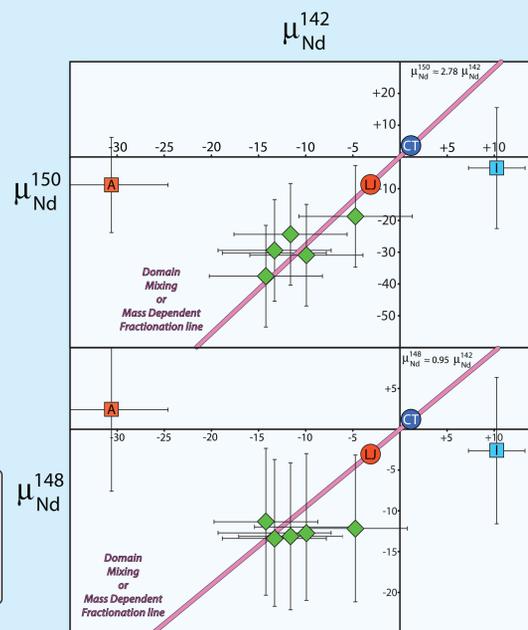


Figure 4: Variations in ^{142}Nd (in parts per million) against variations in ^{150}Nd and ^{148}Nd for averages, compiled from literature, of Allende (A) and Isua (I), and for terrestrial samples where negative ^{142}Nd anomalies have been reported to reflect a signature of the early enriched reservoir. These samples, contrary to Allende and Isua, also show negative ^{150}Nd and ^{148}Nd anomalies, suggesting that the ^{142}Nd variations are not radiogenic in origin, but instead caused by either domain mixing on the filament or mass dependent stable Nd fractionation (natural, or lab induced), both of these processes yield the same relationship in mass-bias corrected data. Also shown are calculated compositions for La Jolla Nd (LJ) and Caltech nNd- β (CT) when normalized to JNd-i. Diagram modified from [12]. Data sources [6,13-16]

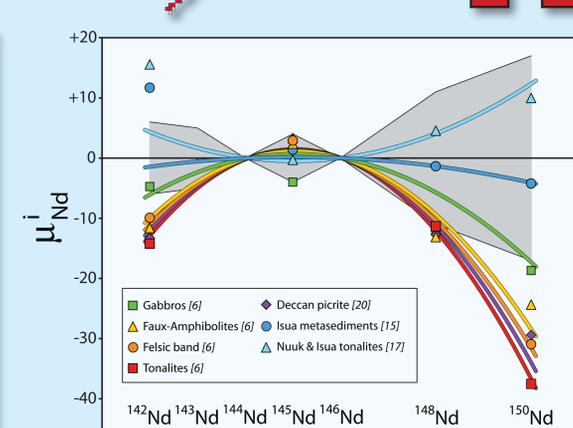


Figure 5: Full Nd isotopic diagram for terrestrial samples showing ^{142}Nd anomalies. Sample averages from Isua (blue) show excess ^{142}Nd not correlated with variations in ^{148}Nd and ^{150}Nd . All samples exhibiting negative ^{142}Nd values also appear to have negative ^{148}Nd and ^{150}Nd values. Also shown are best-model-fit curves of parabolic form for either domain mixing or mass dependent Nd variations. For any sample with negative ^{142}Nd the fit is almost perfect. Interestingly the difference in ^{142}Nd for the Isua samples can be explained by domain mixing or stable isotope fractionation and may not have any chronological or mantle source composition implications. The grey area indicate common uncertainties for static-mode measurements, and highlights the need for reliable ^{150}Nd data to evaluate the origin of ^{142}Nd anomalies.

in ^{148}Nd and ^{150}Nd and do not appear to be radiogenic in origin. Using a normalizing value closer to the true value should lessen the problems with apparent anomalies caused by temporal sample heterogeneity during analysis. Though great effort must still be taken to ensure that sample and standards behave similarly during analysis, this is best done by devoting equal analysis time to ^{142}Nd and ^{150}Nd , as these are the two Nd isotopes most affected by domain mixing and mass dependent isotopic fractionation effects.

Conclusions

The stable isotopic compositions of different Nd isotopic standards differ, and none appear to have a $^{146}\text{Nd}/^{144}\text{Nd}$ ratio of 0.7219. Most have $^{146}\text{Nd}/^{144}\text{Nd}$ ratios of 0.7227. Updating the normalizing ratio do not affect relative differences between samples and standards much, but will lessen the apparent anomalies for samples not following the fractionation behavior of the standards [3,4]. The presence of variations in the stable Nd isotopic compositions of geological samples BCR-2 and BHVO-2, suggest that the variations seen in the Nd isotopic composition of standards may be due to their source rather than their processing, and it highlights the necessity of measuring ^{148}Nd and ^{150}Nd to a relative precision comparable to that obtained for ^{142}Nd , in order to ensure that small variations in ^{142}Nd as observed (e.g. [6, 18-20]) are radiogenic in nature and are not the result of stable isotope variations either from instrumental or natural fractionation, as has been shown for [19-20].

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References

- [1] Kinoshita N. et al. (2012) Science, 335, 1614-1617.
- [2] Boyet M. et al. (2010) EPSL, 291, 172-181.
- [3] Upadhyay D. et al. (2008) JAAS, 23, 561-568.
- [4] Andreasen R. & Sharma M. (2009) IJMS, 285, 49-57.
- [5] Dubois J. C. et al. (1992) IJMS, 120, 163-177.
- [6] O'Neil J. et al. (2008), Science, 321, 1828-1831.
- [7] Lugmair G. W. & Carlson R. W. (1978) LPSC, IX, 689-704.
- [8] Wasserburg G. J. et al. (1981) GCA, 45, 2311-2323.
- [9] Tanaka T. et al. (2000) ChemGeol, 168, 279-281.
- [10] Moore L. (1978) ICGIG, 301-302.
- [11] Hart S. R. & Zindler A. (1989) IJMS, 89, 289-301.
- [12] Andreasen R. & Sharma M. (2009) Science, 325, 267.
- [13] Boyet M. & Carlson R. W. (2005) Science, 309, 576-581.
- [14] Andreasen R. & Sharma M. (2006) Science, 314, 806-809.
- [15] Caro G. et al. (2006) GCA, 70, 164-191.
- [16] Rankenburg K. et al. (2006) Science, 312, 1369-1372.
- [17] Bennett V. et al. (2007) Science, 318, 1907-1910.
- [18] Rizo H. et al. (2012) Nature, 491, 96-100.
- [19] Upadhyay D. et al. (2009) Nature, 459, 1118-1121.
- [20] Andreasen R. & Sharma M. (2004), GCA, 68, 747.