

THE ABSOLUTE NEODYMIUM ISOTOPIC COMPOSITION OF STANDARD MATERIALS – IMPLICATIONS FOR ACCURATE AND PRECISE 142 -NEODYMIUM MEASUREMENTS AND CHRONOLOGY. R. Andreasen¹ and T. J. Lapen¹, ¹Department of Earth and Atmospheric Sciences, University of Houston, 312 Science and Research Building 1, Houston TX 77204, USA (randreas@central.uh.edu).

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 re-determined 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 ^{148}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 make it possible to simul-

taneously 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 don't vary significantly in their fractionation behavior.

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 1 shows the stable Nd isotopic compositions of the four isotopic standards normalized to ^{146}Nd (in the middle and interference free) and JNd-i.

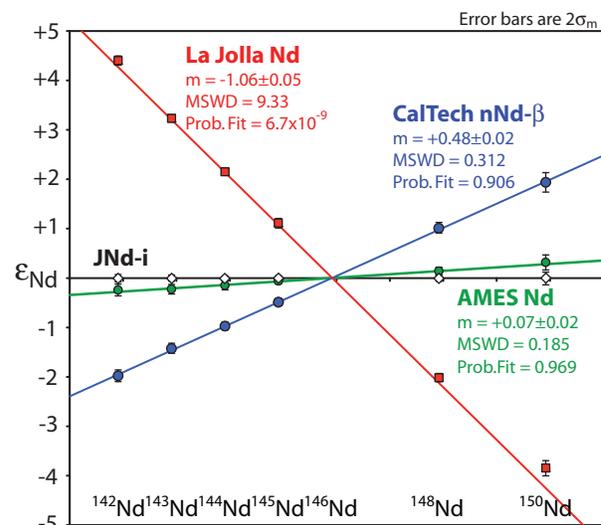


Figure 1: Stable Nd isotopic composition of four isotopic standards normalized to ^{146}Nd and with La Jolla Nd, Caltech nNd- β , and AMES Nd normalized to JNd-i.

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 doesn't 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.

Level of isobaric interferences. The levels of isobaric 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-Nd- 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 enough Sm detectable by Faraday.

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 2; BCR-2 is identical within error to JNd-i in its isotopic composition, whereas BHVO-2 is identical 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 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.

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. Normalizing Caltech-Nd- β to a $^{146}\text{Nd}/^{144}\text{Nd}$ ratio of 0.7227 gives $^{142}\text{Nd}/^{144}\text{Nd} = 1.140552$, $^{143}\text{Nd}/^{144}\text{Nd} = 0.511606$, $^{145}\text{Nd}/^{144}\text{Nd} = 0.348593$, $^{148}\text{Nd}/^{144}\text{Nd} = 0.242110$, $^{150}\text{Nd}/^{144}\text{Nd} = 0.237096$. These updated ratios do not

affect relative differences between samples and standards much, but 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 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, 15-17]) are radiogenic in nature and are not the result of stable isotope variations either from instrumental or natural fractionation, as has been shown for [16-17].

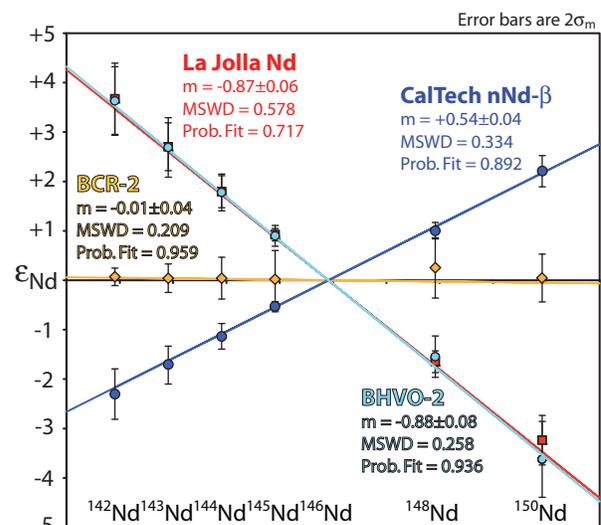


Figure 2: Stable Nd isotopic composition of La Jolla Nd, Caltech nNd- β , and USGS rock standards BCR-2 and BHVO-2 normalized to ^{146}Nd and JNd-i. JNd-i measurements for this session are omitted for clarity.

Acknowledgements: Funding for this project came from the NASA Mars Fundamental Research Program.

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. and 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. and 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) *ICGCI*, 301-302. [11] Hart S. R. and Zindler A. (1989) *IJMS*, 89, 289-301. [12] Andreasen R. and Sharma M. (2009) *Science*, 325, 267. [13] Boyet M. and Carlson R. W. (2005) *Science*, 309, 576-581. [14] Andreasen R. and Sharma M. (2006) *Science*, 314, 806-809. [15] Rizo H. et al. (2012) *Nature*, 491, 96-100. [16] Upadhyay D. et al. (2009) *Nature*, 459, 1118-1121. [17] Andreasen R. and Sharma M. (2004), *GCA*, 68, 747.