

DEVELOPMENT OF A RESONANCE IONIZATION METHOD FOR ISOTOPIC ANALYSIS OF NEODYMIUM AT TRACE LEVELS IN PRESOLAR SiC GRAINS. N. Liu^{1,2,3}, M. R. Savina^{2,3}, and A. M. Davis^{1,2,4}, I. Shkrob⁵, T. Marin⁶, M. Pellin^{1,2,3}, D. G. Willingham³, ¹Department of the Geophysical Sciences, The University of Chicago, Chicago, IL 60637, USA, ²Chicago Center for Cosmochemistry, ³Materials Science Division, Argonne National Laboratory, Argonne, IL 60439, USA, ⁴Enrico Fermi Institute, The University of Chicago, Chicago, IL 60637, USA; ⁵Chemical Sciences and Engineering Division, Argonne National Laboratory, Argonne, IL 60439, USA, ⁶Chemistry Department, Benedictine University, Lisle, IL 60532, USA. (lnsmile@uchicago.edu)

Introduction: Due to limitations of spectroscopic astronomical observations, presolar grains become a precious tool to study nucleosynthesis in individual stars. For more than 20 years, isotopic anomalies in light elements ($A < 56$) in presolar SiC grains have been extensively analyzed by secondary ion mass spectrometry (SIMS) [1-3]. According to these studies, about 90% of presolar SiC grains are mainstream grains that originated from low mass asymptotic giant branch (AGB) stars [1-3].

Isotopic compositions of the rare earth elements (REEs) in mainstream grains can constrain free parameters in *s*-process modeling of AGB stars, since a number of branching points in this region are sensitive indicators of neutron density and temperature in the helium intershell [4]. Previous measurements of REEs have been done with SIMS [5,6], and Inductively Coupled Plasma Mass Spectrometry (ICP-MS) [7]. A limitation of these measurements is isobaric interferences in the region of REE, which obscure the interpretation of the data. Resonance Ionization Mass Spectrometry (RIMS) can analyze isotopes of REEs with the advantage of resonantly ionizing specific elements while suppressing isobaric interferences from others.

Nd mainly records *s*-process isotopic signatures affected by physical conditions during nucleosynthesis in AGB stars. We choose to measure the isotopic composition of neodymium (Nd) in single presolar SiC grains, for several reasons. First, large (3-5 μm , KJH fraction) SiC grains separated from the Murchison meteorite have enough Nd atoms in a single grain to allow measurement of their isotope ratios. Second, Nd has multiple stable isotopes that are produced by distinct nucleosynthetic processes and each isotope has components contributed from these processes by different percentages. For instance, ¹⁴⁴Nd is a pure *s*-process nucleus while ¹⁵⁰Nd is pure *r*-process. Third, so far, only a few branch points in the *s*-process nucleosynthesis path (points where neutron capture and beta decay both have significant rates) have been determined with sufficient accuracy that they can be used to derive sufficiently stringent constraints [4]. Among these are the branchings in the region of the rare earth elements (e.g., ¹⁴²Nd), which all have well-defined abundances. Thus, we can study the *s*-process in mainstream grains and the *r*-process in X grains by

measuring isotopic patterns of the same element. Isotopic abundances in presolar grains can be compared with spectroscopic measurements, which eventually should allow a much fuller understanding of the nucleosynthetic origin of these elements in the Galaxy.

Experimental: We have developed resonant ionization methods to measure REE isotopic compositions in individual presolar SiC grains with CHARISMA [8,9] at Argonne National Laboratory. We used Ti:Sapphire lasers tunable from 700 to 1000 nm; harmonics of the fundamental wavelengths can be formed to produce shorter wavelengths [9]. We have recently developed new Ti:Sapphire lasers to produce much more powerful beams with broader bandwidth (~ 10 pm) in order to solve the problem of the big isotope shifts of REEs and other heavy elements, which had previously limited the precision of RIMS measurement [11].

Fig. 1 shows the resonance ionization scheme we developed for Nd. The excitation step (λ_1) is a resonant transition from the ground state to an excited state and the ionization step (λ_2) is a transition from the excited state to an autoionizing state. Nd exhibits a number of autoionization transitions near the ionization potential [10]. Thus, we fixed λ_1 and scanned λ_2 to maximize Nd signals measured on pure Nd metal. We chose $\lambda_2 = 463.495$ nm based on maximum signal levels (Fig. 2) and stability of isotope ratios.

Nd Isotopic Analysis of Standards: In order to resonantly ionize Nd we need to produce gas phase ground-state neutral atoms from the samples. Rare earth elements generally form strong bonds with oxygen which are difficult to break with the ion or laser beams used to liberate material from samples, resulting in low useful yields even when analyzing “pure” metals. This is not an issue for SiC presolar grain analysis, since SiC is a highly reduced mineral phase with little or no oxygen present. For metal analysis we use a pulsed Ga⁺ gun to desorb Nd neutral atoms from the surface at a repetition rate of 1 kHz, with additional Ga⁺ pulses applied between analysis pulses to keep the analyzed spot free of oxides, which form at a noticeable rate due to water adsorption even in ultrahigh vacuum ($2\text{-}3 \times 10^{-9}$ torr in our system). Results for Nd metal isotopic analysis at the 95% confidence limit are shown in Table 1.

In addition to Nd metal, we analyzed low-concentration standards consisting of Diphonix and

TRU ion exchange resin beads (Eichrom, inc.) containing 10 to 100 ppb each of Nd, Gd, Eu, and Sm. Results for Diphonix beads at 100 ppb loading are shown in Table 2, normalized to ratios of pure metal given in Table 1. Instead of a Ga⁺ gun, a pulsed laser was used to vaporize material. NdO_x peaks were absent in these spectra (they are never completely suppressed from metals even with the Ga⁺ pulse sequencing described above), showing that REEs in these beads are reduced as they are in SiC. Further, isobaric interference from other REEs (Sm in this case) was completely absent.

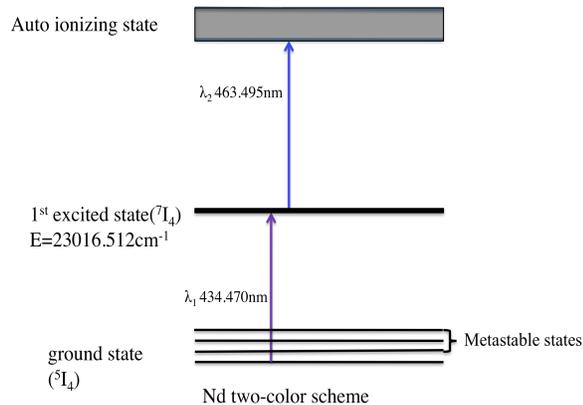


Fig. 1 Neodymium resonance ionization scheme. The wavelengths (in vacuum) for different transitions are labeled along the transitional lines. Metastable states above ground state are low-lying thermally populated levels.

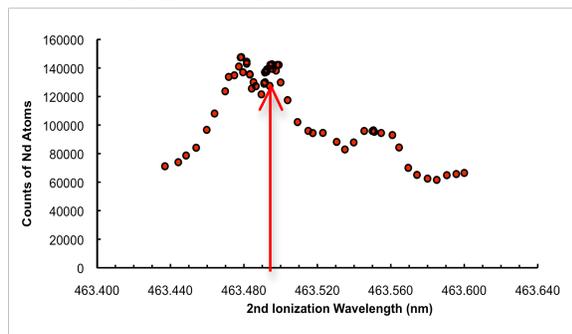


Fig 2. Neodymium ion signal as a function of wavelength of the ionization transition step from the ⁷I₄ excited state at 23016.512cm⁻¹ (Fig. 1). The arrow indicates the wavelength chosen for the final resonance ionization scheme.

Results: Isotopic ratios of pure metal show small isotope shift effects, which may explain the positive ratios of light isotopes and negative ratios of heavy isotopes. The effect is generally smaller on beads, possibly due to the lower velocity of laser-desorbed atoms compared to ion sputtering, which lowers the Doppler broadening of the gas phase material and suppresses off-resonance excitation of isotopes outside the bandwidth of the Ti:Sapphire lasers. Larger data sets (i.e. at higher preci-

sion) are required to make a definitive conclusion. Neodymium isotope ratios measured on resin beads generally agree with those from metal supported by the close to zero ratios with 95% confidence in Table 2, though the heaviest and lightest isotopes do not quite agree at the 95% confidence level. This may also be due to a difference in the desorption method. However, since the expected isotopic anomalies in presolar SiC are generally >100‰ or <-100‰ (R. Gallino, *pers. comm.*) and the absolute fractionations seen here are much smaller than that they can be easily normalized at the required level. The method is therefore sufficiently robust and has enough precision to be applied to analysis of presolar SiC grains.

References: [1] Hoppe P. et al. (1994) *ApJ*, 430, 870-890; [2] Nittler L. R. (2003) *EPSL*, 209, 259-273; [3] Hoppe P. et al. (2010) *ApJ*, 719, 1370-1384; [4] Best J. et al. (2001) *Phys. Rev. C* 64, 015801-15; [5] Zinner E. et al. (1991) *ApJ* 382, 47-50; [6] Terada K. et al. (2006) *New Astron. Rev.* 50, 582-586; [7] Yin Q et al. (2006) *ApJ*, 606, 592-604; [8] Savina M. R. et al. (2003b) *LPS* 34, #2079; [9] Savina M. R. et al. (2003a) *GCA* 67, 3201-3214; [10] Worden E. F. et al. (1977) *ApJ* 466, 109-113; [11] Isselhardt B. H. et al. (2011) *Anal Chem* 83, 2469-2475.

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Table 1 Isotopic analysis of Nd metal. Delta units (ppt deviation) are normalized to ¹⁴⁴Nd and terrestrial ratios. 95% confidence limit includes both statistical and non-statistical errors.

Isotope	Ratio(‰)	95% C.L.
δ ¹⁴² Nd	22.4	12.1
δ ¹⁴³ Nd	31.5	10.5
δ ¹⁴⁵ Nd	11.0	13.1
δ ¹⁴⁶ Nd	-20.5	8.9
δ ¹⁴⁸ Nd	-14.9	12.7
δ ¹⁵⁰ Nd	-28.2	19.6

Table 2 Isotopic analysis of a 90 mm Diphonix resin bead containing 100 ppb each of Nd, Gd, Eu, and Sm. Delta units are normalized to ¹⁴⁴Nd and ratios in Table 1. . Units and confidence limits as in Table 1.

Isotope	Ratio (‰)	95% C. L.
δ ¹⁴² Nd	-21.2	21
δ ¹⁴³ Nd	-14.9	27.3
δ ¹⁴⁵ Nd	35.4	53.3
δ ¹⁴⁶ Nd	18.2	21.3
δ ¹⁴⁸ Nd	19.2	29.5
δ ¹⁵⁰ Nd	45.5	42.7