

**NO  $^{142}\text{Nd}$  EXCESS IN THE EARLY ARCHEAN ISUA GNEISS IE 715-28.** D. A. Papanastassiou<sup>1, 2</sup>, M. Sharma<sup>3</sup>, H. H. Ngo<sup>2</sup>, G. J. Wasserburg<sup>2</sup>, and R. F. Dymek<sup>4</sup>, <sup>1</sup>Earth and Space Sciences Div., M/S 183-335, JPL, Caltech, 4800 Oak Grove Drive, Pasadena, CA 91109-8099, <sup>2</sup>The Lunatic Asylum, Div. Geol. and Planet. Sciences, M/C 170-25, Caltech, Pasadena, CA 91125, <sup>3</sup>Dept. of Earth Sciences, Dartmouth College, Hanover, NH 03755, <sup>4</sup>Dept. Earth and Planet. Sciences, Washington Univ., St. Louis, MO 63130 (dap@mail1.jpl.nasa.gov)

There is abundant evidence for the existence of  $^{146}\text{Sm}$  in the early solar system and for preservation of effects in the  $^{146}\text{Sm}$ - $^{142}\text{Nd}$  system in differentiated meteorites ([1]; see recent discussion in Stewart et al. 1994). Information from the  $^{182}\text{Hf}$ - $^{182}\text{W}$  system, as revised by new careful work [2-3] also indicates that the Earth's core formed relatively early. It is in principle possible for early-formed crust and mantle reservoirs on Earth to have preserved evidence for  $^{146}\text{Sm}$  if such reservoirs were produced with high Sm/Nd fractionation and if they have remained isolated and closed since  $\sim 4.3$  Ga. The mean life of  $^{146}\text{Sm}$  of 149 Ma is sufficiently long to make this an intriguing possibility. Harper and Jacobsen [4] reported a  $33 \mu$  ( $\mu$  = parts per million) excess  $^{142}\text{Nd}$  in a 3.8 Ga felsic gneiss (IE 715-28) from Isua, West Greenland. In a previous paper [5] we attempted to confirm the data on  $^{142}\text{Nd}$  reported by [4]. The investigations of Harper and Jacobsen [4] and of Sharma et al. [5] were performed using F/MAT 262 mass spectrometers, with multiple ion beam collection. In the work of Sharma et al., an attempt was made to document the requisite precision in the Nd isotope ratio determinations. For this purpose, Nd standards were made up with 0, 30, and  $57 \mu$  excesses in  $^{142}\text{Nd}$ . Specific data collection techniques (in the static mode) were investigated. The observations indicated that relatively large effects (up to  $60 \mu$ ) could be obtained for Nd standards based on the positioning of the sample filament and on the ion source focusing potentials. These shifts were found to be systemic and not reproducible. For the work on the F/MAT 262 we established a standard operating procedure (SOP) but found that even its consistent use did not prevent isotope shifts in  $^{142}\text{Nd}/^{144}\text{Nd}$ , of a magnitude similar to the effect under investigation. The conclusion was that further refinements in mass spectrometric techniques were necessary, in order to determine whether the reported effects were real. It has always been possible that the systemic shifts in  $^{142}\text{Nd}/^{144}\text{Nd}$  in our earlier work were specifically associated with the design of our instrument, which included a 2<sup>nd</sup> stage, for high abundance sensitivity measurements. In particular, alignment slits at the entry and exit of the instrument mass analyzer magnet, which were not precisely locatable in the vertical axis, may have contributed to the observed shifts. The successor instrument to the F/MAT 262, the ThermoFinnigan Triton, has been

installed and become operational in the new geochemical analytical facilities at JPL. We have established that analyses of Nd yield reproducible measurements  $^{142}\text{Nd}/^{144}\text{Nd}$  at the of precision of  $9 \mu$  ( $2 \sigma$  confidence level, for the distribution of Nd standard runs). The analytical procedures include: a) measurement of large samples of Nd (300-500 ng) on a double-Re-filament assembly; b) high intensity  $\text{Nd}^+$  ion beams ( $4.5 \times 10^{-11}$  A for  $^{144}\text{Nd}^+$ ); c) amplifier "rotation" through the Faraday cups, as provided on this instrument; d) daily (at night) gain calibrations; e) ion beam background measurements, every set of 20 ratios, through the deflection of the ion beam at the source exit slits (e. g., as contrasted with closing the ion beam valve or changing the magnetic field); f) collection of 180 isotope measurements, under static conditions and with an integration interval of  $\sim 60$  seconds; g) elimination of potential Ce and Sm interferences through multiple clean-up passes of the Nd-cut through the ion exchange chemistry; and h) clean-up of organics in the final Nd cut by using intense UV light.

The results for  $^{142}\text{Nd}$  are shown in Fig. 1. Analyses of samples of the IE 715-28 felsic gneiss sample were interspersed with analyses of the Nd beta standard, which serves as the reference,  $0 \mu$  standard. This material was obtained from the Ames Laboratory, Iowa, and has been used for standard measurements, following the generation and calibration of standards,  $\sim 20$  years ago [6]. We have dissolved one sample of IE 715-28 and have concluded analyses of aliquots loaded on three double filament assemblies. For the Nd beta,  $0 \mu$  standard, we have obtained multiple analyses on about one dozen filament loads. We have performed, at this time, a single analysis of the  $30 \mu$  standard. In Fig. 1, the analyses of the Nd beta standard ( $0 \mu$  standard) define a  $2\sigma$  range of  $9 \mu$  for the  $^{142}\text{Nd}/^{144}\text{Nd}$  precision. The data have been normalized using  $^{146}\text{Nd}/^{142}\text{Nd} = 0.636151$ , as this reduces the error propagation due to the isotope mass fractionation. There is no ambiguity in the use of  $^{146}\text{Nd}/^{142}\text{Nd}$  for isotope fractionation even for samples, which may exhibit an effect in  $^{142}\text{Nd}/^{144}\text{Nd}$  (excess or deficit). For the isotope fractionation correction, we have used the Triton programs, which (as we have checked) use effectively an exponential law [7]. The analysis of the  $30 \mu$  standard is very well resolved, with the data

precision achieved. An effect of  $\sim 30$   $\mu$  in  $^{142}\text{Nd}/^{144}\text{Nd}$  in the Isua sample would be well resolved. The three analyses of the IE 715-28 Isua sample are not distinguishable from the analyses of the Nd beta standard. For the analyses of the Nd 0  $\mu$  standard, we obtained reproducibility for  $^{145}\text{Nd}/^{144}\text{Nd}$  of  $\pm 7$  ppm (with the  $^{145}\text{Nd}$  centered in the center Faraday cup). Similarly, for  $^{143}\text{Nd}/^{144}\text{Nd}$  the observed range was  $\pm 5$  ppm. Therefore, the data for Nd isotopes collected in Faraday cups close to the central ion optical axis are well-behaved, as are the data for  $^{142}\text{Nd}/^{144}\text{Nd}$ . However, for the heavier isotopes,  $^{148}\text{Nd}$  and  $^{150}\text{Nd}$ , we observed larger and correlated shifts, up to nearly 100  $\mu$ . In Fig. 2, we show deviations during these experiments obtained for  $^{148}\text{Nd}/^{144}\text{Nd}$  and  $^{150}\text{Nd}/^{144}\text{Nd}$  (also normalized using  $^{146}\text{Nd}/^{142}\text{Nd}$ ). These effects are correlated and are artifacts. Similar (and slightly larger) effects in the measurements of these isotope ratios were observed also in our earlier study, using the F/MAT 262 mass spectrometer [5]. Part of the effects in these ratios may be caused by lower precision due to the lower abundance of  $^{148}\text{Nd}$  and  $^{150}\text{Nd}$ . However, it is most likely that the effects are due to the focusing characteristics (presumably in the Z-direction) for instruments with non-normal magnet exit pole faces relative to the ion beams. For our data collection,  $^{145}\text{Nd}$  is centered in the center cup, so that  $^{142}\text{Nd}$  and  $^{148}\text{Nd}$  are each 3 mass units away from the optic axis. Therefore, there is, in principle, concern about artifacts also in  $^{142}\text{Nd}/^{144}\text{Nd}$ . Such artifacts are not reflected in the data, and we must assume that, apparently this effect is stronger for the heavier mass region relative to the center cup. This effect requires serious investigation, by ion optics experts.

Based on these results we do not confirm the report of excess  $^{142}\text{Nd}$  in the one Isua felsic gneiss we have re-measured with significantly improved precision. Indeed, the Nd isotope data appear to be consistent with recent Hf isotopes measurements on early Archean zircons, which show no evidence of a depleted mantle in the Hadean [8]. Our results are in contrast,

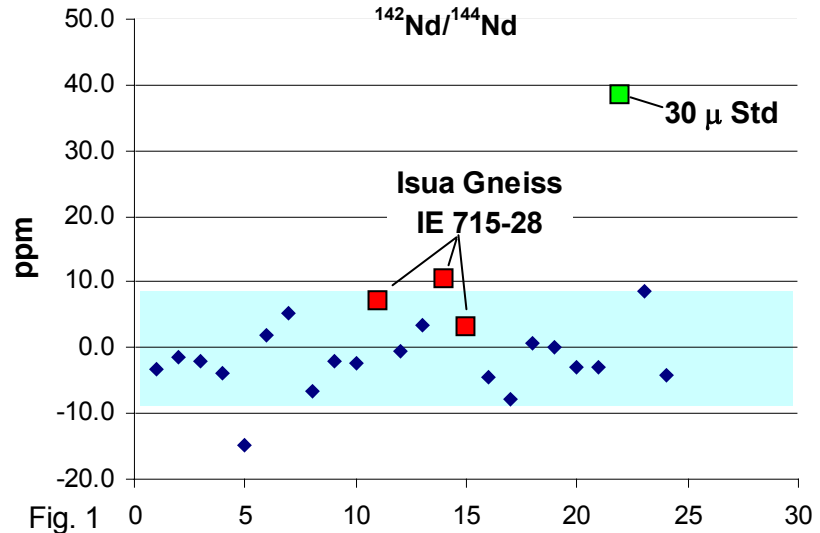


Fig. 1

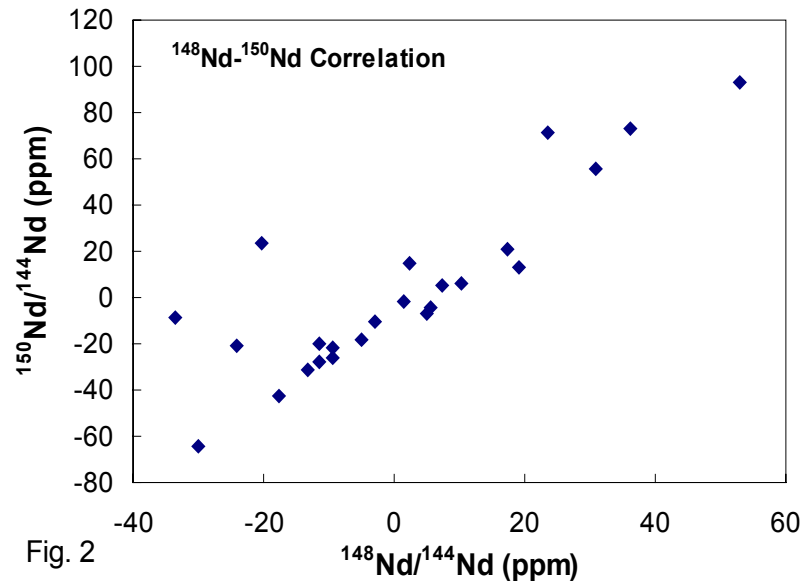


Fig. 2

however, to the reports of  $^{142}\text{Nd}$  excesses in early Archean rocks [9-10]. We intend to extend our measurements to other samples and to more extensive measurements of the gravimetric isotopic standards with known  $^{142}\text{Nd}$  excesses.

**References:** [1] Prinzhofer et al. (1992) *GCA* **56**, 797-815. [2] Yin et al. (2002) *Nature* **418**, 949-952. [3] Kleine et al. (2002) *Nature* **418**, 952-955 [4] Harper & Jacobsen (1992) *Nature* **360**, 728-732 [5] Sharma et al. (1996) *GCA* **60**, 2037-2047 [6] Wasserburg et al. (1981) *GCA* **45**, 2311-2323. [7] Russell et al. (1978) *GCA* **42**, 1075-1090 [8] Amelin et al. (1999) *Nature* **399**, 252-255 [9] Boyet et al. (2002) *GCA* **66**(15A), A99 [10] Caro et al (2002) *GCA* **66**(15A), A120. This work was supported by NASA Cosmochemistry RTOP 344-31-55-01. Div. Contr. 8904(1106).