COUPLED $^{142}$Nd,$^{144}$Nd and $^{176}$Hf ISOTOPIC DATA FROM 3.6 -3.9 Ga ROCKS: NEW CONSTRAINTS ON THE TIMING AND COMPOSITION OF EARLY TERRESTRIAL CHEMICAL RESERVOIRS.

Vickie C. Bennett¹, Alan D. Brandon², Joe Hiess³, and Allen P. Nutman³, ¹Research School of Earth Sciences, The Australian National University, Mills Rd. Bldg. 61 Canberra, Australia 0200, vickie.bennett@anu.edu.au, ²NASA Johnson Space Center, Mailcode KR, 2101 NASA Road One, Houston, TX 77058, alan.d.brandon@nasa.gov
³Institute of Geology, Chinese Academy of Geological Sciences, 26 Baiwanzhuang Road, Beijing, 100037, P.R. China, nutman@bjshrimp.cn

Introduction: Increasingly precise data from a range of isotopic decay schemes, including now extinct parent isotopes, from samples of the Earth, Mars, Moon and meteorites are rapidly revising our views of early planetary differentiation. Recognising $^{142}$Nd isotopic variations in terrestrial rocks (which can only arise from events occurring during the lifetime of now extinct $^{146}$Sm [$t_1/2=103$ myr]) has been an on-going quest starting with Harper and Jacobsen [1]. The significance of $^{142}$Nd variations is that they unequivocally reflect early silicate differentiation processes operating in the first 500 myr of Earth history, the key time period between accretion and the beginning of the rock record. The recent establishment of the existence of $^{142}$Nd variations [2,3] in ancient Earth materials has opened a new range of questions including, how widespread is the evidence of early differentiation, how do $^{142}$Nd compositions vary with time, rock type and geographic setting, and, combined with other types of isotopic and geochemical data, what can $^{142}$Nd isotopic variations reveal about the timing and mechanisms of early terrestrial differentiation? To explore these questions we are determining high precision $^{142}$Nd, $^{143}$Nd and $^{176}$Hf isotopic compositions from the oldest well-preserved (3.63- 3.87 Ga), rock suites from the extensive early Archean terranes of southwest Greenland and western Australia.

Methods: Samples for analysis are selected based on field relationships, age and trace element characteristics. The ages of all felsic samples are determined by U-Pb zircon dating using SHRIMP; ages of mafic samples are determined from cross cutting relationships of dated felsic samples. $^{142}$Nd/$^{144}$Nd isotopic compositions were measured on a Triton thermal ionization mass spectrometer at the Johnson Space Center using a multidynamic data collection scheme modified from [4]. Fourteen measurements of an AMES Nd solution run interspersed with the samples yielded a 2 SD external reproducibility of ±3.3 ppm (in-run precisions were typically <2ppm). Hf isotopic compositions were determined on single zircons separated using standard heavy liquid density methods from splits of whole rocks used for Nd measurements. All zircons were characterized by cathodoluminescence imaging and ages for each zircon determined by U-Pb isotopic analyses using the ANU SHRIMP RG, prior to Lu-Hf isotopic measurements on a Neptune MC-ICPMS coupled to an Excimer (193 nm) laser following methods described in [5].

Results and Discussion: High precision $^{142}$Nd isotopic data were obtained from 17 samples from the Itsaq complex, southwest Greenland (which includes the Isua supracrustal belt and Akilia island) and the Narryer gneiss complex, western Australia. Itsaq complex samples range in age from 3.63-3.87 Ga and include both felsic and mafic lithologies. The 3.73 Ga gneisses from the Narryer gneiss complex are the oldest rocks in the Yilgarn craton. The Itsaq samples have $^{142}$Nd/$^{144}$Nd compositions that are 8-17 ppm higher than modern terrestrial compositions and with the 5 ca. 3.85 Ga gneisses yielding similar values of +15ppm. The new results confirm and extend the high precision (< +/-5 ppm) data of Caro et al. [4]. The 3.73 Ga gneisses from the Narryer gneisses overlap in age with the Itsaq samples, but have distinctly lower $^{142}$Nd/$^{144}$Nd compositions of +4 ppm (Fig. 1). The most positive isotopic compositions from the southwest Greenland samples tend to decrease with younger ages suggesting either increasing isolation, or eradication, of the positive high $^{142}$Nd source.

Fig. 1. $^{142}$Nd/$^{144}$Nd variations (expressed as ppm differences from modern terrestrial compositions) as a function of age in early Archean rocks from southwest Greenland (Itsaq complex), western Australia (Yilgarn Craton) and South Africa (Barberton). Data from this study and [4].

The combined $^{143}$Nd- $^{142}$Nd data forms a self-consistent dataset, with the Itsaq samples having both higher $^{142}$Nd/$^{144}$Nd and initial $^{142}$Nd/$^{144}$Nd isotopic compositions than the Narryer gneisses. The relative isotopic differences preserved in contemporaneous
samples from two widely separated terranes points to the existence of diverse mantle sources at 3.7 Ga. The Narryer gneisses either formed from a mantle source with a lower average Sm/Nd than the Itsaq source, or the Narryer mantle was partially remixed with a more LREE enriched source prior to 3.7 Ga, but after $^{146}$Sm was largely decayed.

Data from the coupled short and long half-life $^{146}$Sm-$^{142}$Nd and $^{147}$Sm-$^{143}$Nd decay schemes allows calculation of a mantle source differentiation age [cf.1]. Assuming a 20 ppm terrestrial offset from average chondritic compositions [6,7] and a solar system initial $^{146}$Sm/$^{144}$Nd of 0.0075, with solar system evolution starting at 4.567 Ga, the combined $^{143}$Nd- $^{142}$Nd data from the oldest (ca. 3.85 Ga) measured terrestrial samples require formation of differentiated silicate reservoirs in the first 30-60 myr of Earth history.

The most positive initial Hf isotopic compositions from zircons from three of the same samples yielding positive $^{142}$Nd anomalies are all within error of chondritic values (calculated using $\lambda^{176}$Lu = 1.867 x 10$^{-11}$ yr$^{-1}$). These results are in agreement with previously published whole rock and bulk zircon results (Fig. 2) for Archean samples from west Greenland, when all are calculated using the same decay constant and chondritic parameters. They span a much narrower compositional range and are distinct from the more heterogeneous initial $\varepsilon$Hf values exhibited by the 4.0-4.4 Ga Jack Hills zircons [4].

![Fig. 2. Initial Hf isotopic compositions for early Archean (3.6-3.9 Ga) rocks from southwest Greenland (Itsaq complex) including three samples with positive $^{142}$Nd isotopic anomalies. Also shown are data from Pilbara, Barberton and Jack Hills localities. Data sources: squares-this study, colored circles-[10,11], black circles [5].](2139.pdf)

**The Composition of Early Silicate Reservoirs:** The $^{142-143}$Nd and initial $^{176}$Hf isotopic compositions of early Archean rocks define the time-average Lu/Hf and Sm/Nd of their mantle source regions. Generation of +36 ppm positive $^{142}$Nd anomalies relative to chondritic compositions [6,7] as well as $^{143}$Nd = ca. +3 in 3.85 Ga samples, requires an early formed high Sm/Nd reservoir. In contrast, the near chondritic initial $^{176}$Hf/$^{177}$Hf compositions from the same early Archean samples indicate a source with a time averaged chondritic Lu/Hf ratio. Thus the trace element composition of the pre-3.85 Ga terrestrial depleted mantle differs from the MORB source mantle, which is characterized by both supra-chondritic Lu/Hf and Sm/Nd. Significantly this means that average continental crust cannot be the primary complimentary enriched reservoir to the early depleted mantle (Fig. 3). These observations provide new evidence in support of models for very early (30-60 myr after T$_{E}$) silicate differentiation on the Earth [e.g. 8, 9] unrelated to early continental crust formation.

![Fig. 3. Comparison of early (>3.8 Ga) terrestrial depleted mantle trace element compositions determined from $^{142}$Nd and $^{176}$Hf isotopic data from early Archean rocks, compared with average MORB source depleted mantle (calculated using present day $\varepsilon$Nd =10, $\varepsilon$Hf =+16 and average age of 2 Ga). Also shown is composition of average continental crust.](2139.pdf)