

A PROCEDURE TO CLEANLY SEPARATE SOLAR WIND OSMIUM EMBEDDED IN GENESIS SILICON COLLECTORS. G. Janakiraman Paramasivan¹, M. Sharma¹, A. Jurewicz¹, and D. Burnett². ¹Department of Earth Sciences, 6105 Fairchild Hall, Dartmouth College, Hanover, NH 03755, ²Division of Geological & Planetary Sciences, MS 170-25, Caltech, Pasadena CA 91125.

Introduction: The Re/Os ratio of the solar nebula is not well constrained [1]. Since solar photosphere has been isolated from the nuclear reactions taking place in the solar core, its Re/Os ratio should be the same as that of the solar nebula. The solar Re/Os ratio is not known. While direct measurements of solar Os abundance have been made [2-4], there is only one early attempt to provide an upper limit of Re abundance of 0.015 atoms/10⁶ Si atoms (or 0.01042 µg/g) [5]. This limit appears to be consistent with the "smooth odd mass curve" criterion [6, 7]. Taken at its face value and using the most recent Os abundance determination, we find that the solar Re/Os ratio is <0.0200. In comparison, the Re/Os ratio of CI chondrite Orgueil is 0.0797—at least a factor of four *higher* than the upper limit obtained by analysis of solar spectrum! A direct estimation of the solar Re/Os is therefore needed to provide a benchmark against which early alteration processes on meteorite parent bodies and planetary evolution scenarios could be evaluated.

Genesis-returned solar wind (SW) provides a unique opportunity for determining the time integrated Re/Os ratio. No fractionation of Os or its isotopes during SW formation is predicted: first, the first ionization potential (FIP) of Os is 8.7 eV, which is less than the observed FIP threshold of ~10 eV beyond which elements are noticeably depleted in the corona relative to the photosphere (e.g., [8, 9]); second, calculations for inefficient coulomb drag in these uniformly-heavy isotopes indicate no measurable mass-dependent fractionation (cf. [10]). So, the Genesis SW Os concentration and isotope composition determination, which would also yield a SW Re abundance, will be a direct proxy for the photosphere. The 2-year Genesis array Os fluence is estimated to be 1.3×10^6 Os atoms/cm² (2.2cm²/fg) [11].

Our analysis of different Genesis collector material indicates that Os blank of silicon collectors is low and therefore suitable for Os isotope measurements. However, the measurements are amongst the most challenging. Due to the crash-landing of the Genesis spacecraft, several small fragments of the collectors will need to be combined to make an allocation of only ~ 2.2 cm² of surface area; that is, a maximum of ~1 fg of SW Os (= 3 million atoms of Os) will be available to measure. Of immediate concern is how to clean the collector surface contaminated with terrestrial dust, organic residue, metal, and possibly Si welded onto itself. The cleaning needs to be done in such a way that it does not compromise the SW Os, which has been modeled to be buried

throughout the zone of 15 to 250 nm below the collector surface. In this study we have developed a robust chemical procedure that permits sequential removal of 5-10 nm thick surface layers from silicon wafers. Extensive experimentation combining clean-lab techniques with photolithography and atomic force microscopy was used to obtain these ultrathin films of SiO₂, which were then removed and characterized. We find that by decoupling the oxidation and etching steps we are able to exfoliate the wafer with precision. This will allow us to remove surface contamination.

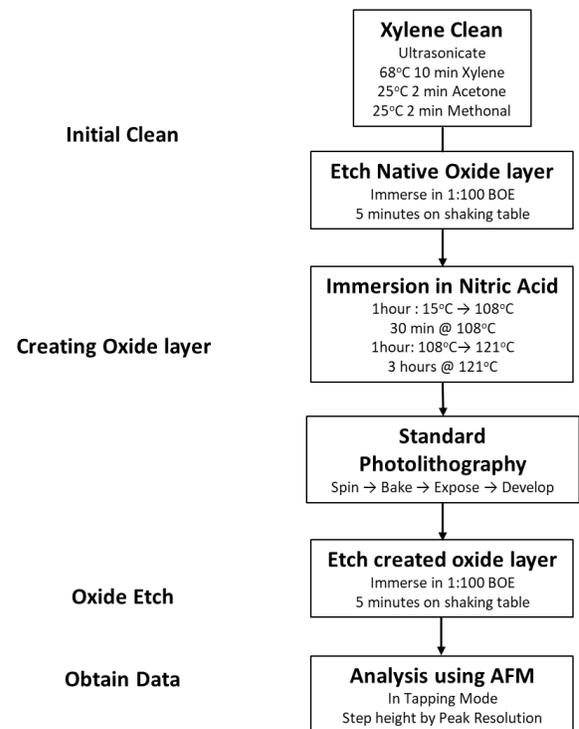


Fig. 1. Flowchart illustrating steps in cleaning, creation and measurement of new oxide layer.

The surface of the flown Genesis wafer is saturated with solar wind H⁺ ions (the major component of the solar wind) mostly implanted at energies ~1-1.5 keV. We discovered that the fluence and energy with which H⁺ ions are implanted in different types of tested wafers (commercial wafer, non-implanted flight spare wafers, implanted Si-plate, H-implanted wafers) exerted a fundamental control on their oxidation. Specifically, different types of wafers gave different etching and oxidation

rates when subjected to the same procedures (e.g., reagents, set up such as ultrasonication for etching, oxidation using nitric acid etc.). The depth of implanted hydrogen layer with respect to the surface seems to be the driver of these variations. This observation implied that flown wafers needed to be used to fine tune the oxidation step in the cleaning procedure.

Due to the small size of flown wafers, especially those allocated for cleaning, a precise evaluation of sequential oxidation and etching procedure in flown wafers cannot be done by direct measurement. We finessed this issue by implanting Nd in Si wafers (flown and flight-spares) at 150 keV (Fluence = 1.42×10^{14} atoms cm^{-2}). The amount of Nd and its isotope composition varies with depth and was characterized using secondary ion mass spectrometry (CAMECA IMF 7f, Caltech, Fig. 2). Oxidation and etching of flown wafers 60116 and 60123 were done and Nd isotopes measured using high sensitivity thermal ionization mass spectrometry (Triton, Dartmouth).

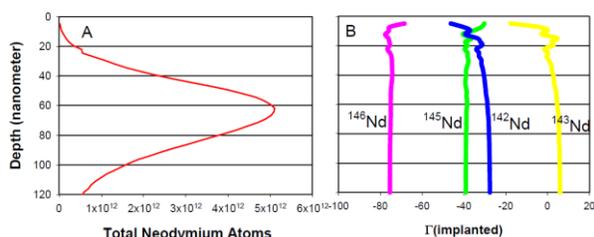


Fig. 2. Depth variations in (A) Nd concentration and (B) Nd isotope composition in the implanted wafers. Γ refers to percent deviations from chondritic reservoir in the implanted Nd isotope composition.

The unique isotope composition of the implanted Nd is far from normal (Fig. 2). Moreover, negligible amounts of ^{148}Nd and ^{150}Nd isotopes are implanted in the wafers. This allowed us to calculate both Nd yield and procedure blank by isotope dilution using a single measurement. The measured stable isotopes of the sequential leaches combined with their Nd yields further permitted us to uniquely estimate their corresponding etch depths.

We oxidized 60116 (area = 0.1 cm^2) by immersing it in HNO_3 for a total of 235 min. The wafer was then implanted with Nd (total implanted Nd = 2.84 ng) and SiO_2 layer removed by etching with acidic bromine solution (ABS, 10M HF + 0.5M HBr + 10mM Br_2) for 5 minutes [12]. Insoluble fluorides were dissolved using a mixture hot HCl and boric acid. The Nd yield and isotope composition and concentration point to oxidation to a depth of $43 \pm 1 \text{ nm}$ in a single step. AFM analysis of the ABS etched wafers shows that the etching surface is not smooth (Fig. 3), which means that Nd

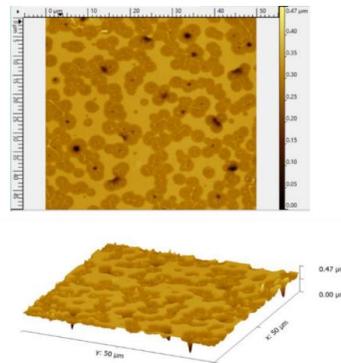


Fig. 3. AFM top and side views of ABS etch pits.

sourced from various layers likely contributed to the etch. We sequentially oxidized and etched wafer no. 60123 (area = 0.074 cm^2) for four different time intervals and find that the wafer etched depths vary: 16 nm (etch 1), 6 nm (etch-2), 6 nm (etch-3), and 14 nm (etch-4). These experiments suggest that we can sequentially oxidize and etch 10 to 15 nm of the top layer of the Si wafers, thereby removing surface contamination. Following this initial etching Os can be extracted from the wafers using the ABS, as is outlined in Fig. 4.

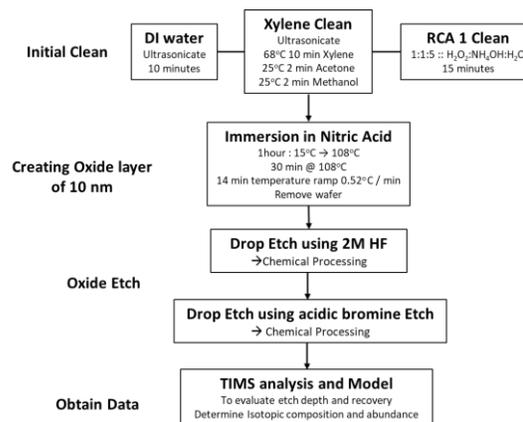


Fig. 4. Possible method to oxidize and clean the top 10 nm of an Si-wafer and then remove Os using ABS.

References: [1] Sharma et al., 2015 LPS XLVI Abstract #2361. [2] Asplund M. et al. (2009), *Annu Rev Astron Astr*, 47, 481-522. [3] Kwiatkowski M. et al. (1984), *Astron Astrophys.*, 135, 59-60. [4] Quinet P. et al. (2006), *Astron Astrophys*, 448, 1207-U93. [5] Swensson J.W. (1970), *Sol Phys*, 13, 25-. [6] Anders E. and Grevesse N. (1989), *GCA*, 53, 197-214. [7] Burnett D.S. et al. (1989), *GCA*, 53, 471-481. [8] Schmelz J.T. et al. (2012), *ApJ*, 755. [9] Burnett et al. (2017) LPS XLVIII Abstract # 1538. [10] Bochsler P. (2007), *Astron Astrophys Rev.*, 14, 1-40. [11] Riesenfeld et al. (2013) *Space Sci. Rev.* 175 125-164 (SOM). [12] Bressers et al. (1996) *J. Electroanal. Chem.*, 406(1), 131-137.