IMPACT OF ACID-CLEANING ON THE SOLAR WIND LAYER OF GENESIS FLIGHT WAFERS – PARTIAL DISSOLUSION AND RECOVERY OF THE LITHIUM-6 IMPLANT.

N. Waeselmann[1], M. Humayun[1], Y.S. Goreva[2], D.S. Burnett[3] and A. Jurewicz[4], [1]National High Magnetic Field Laboratory & Dept. of Earth, Ocean & Atmospheric Science, Florida State University, 1800 E. Paul Dirac Dr., Tallahassee, FL 32310, USA (naemi@magnet.fsu.edu), [2]Smithsonian Institution, Washington, DC 20004, USA; [3]California Institute of Technology, Pasadena, CA, 91125, USA; [4]Center for Meteorite Studies, Arizona State University, Tempe, AZ 85287, USA.

Introduction: Determination of the oxygen isotope composition of the Sun was the top priority for the NASA *Genesis* mission [1]. The successful measurement of oxygen isotopes [2] has triggered a discussion on the role of mass fractionation due to Inefficient Coulomb Drag, ICD [3], that may have displaced the oxygen isotope composition of the solar wind from that of the photosphere. There are other interpretations involving photochemically-induced mass-independent fractionation in the solar wind [4]. These issues can be resolved by determining the Mg isotope composition of the solar wind, which is currently the highest priority objective for the *Genesis* mission. Attempts to determine Mg isotopes *in situ* by back-side depth profiling have not achieved sufficient precision to yield a definitive answer [5], so that precise measurement by bulk analysis of SW-derived Mg is required.

Previously, we reported Mg isotopes on Si-on-sapphire (SoS) wafers [6]. We found a mild, mass-dependent fractionation due to differential implantation of Mg isotopes into the sapphire but no evidence of ICD fractionation. To avoid the problem of differential implantation, a new set of measurements on Si wafers has been undertaken. Si wafers pose two very significant problems. First, the surfaces have to be thoroughly cleaned to remove Mg from UTTR debris. The aggressive acid cleaning procedures devised to clean Genesis flight wafers cause concerns that some of the SW implant may be removed, as well, biasing the δ^{26}Mg to heavier values. Second, unlike with SoS wafers, achieving a quantitative yield of Si is not easy, which could bias the δ^{26}Mg to lighter values. To overcome both of these problems, the wafers under investigation were ion-implanted with ^{6}Li at a fluence about two orders of magnitude higher than that of SW Mg. The ^{6}Li implant was designed to overlay the solar wind layer at a depth of 50–200 nm below the exposed surface.

Methodology: The ^{6}Li implant was performed by Leonard Kroko Inc. at an energy of 15 keV and a beam current of 0.4 µA for a fluence of 3E14 ions/cm^{2}. Figure 1 shows a SIMS depth profile of the ^{6}Li implant.

Samples: **A-5 CZ** is a 1.16cm^{2} non-flight CZ Si wafer used as a ^{6}Li implant control.

60491 and 60500 FZ are flight samples of ~0.2 cm^{2} from a focused study of the effectiveness of aqua regia cleaning [7]. The samples were imaged by ToF-SIMS before and after the cleaning procedure [7]. It should be noted that the surface of 60500 was partially covered with conducting paint during the ^{6}Li implant process.

60493 FZ is a ~0.2 cm^{2} flight sample which was cleaned with boiling sulfuric acid. The ToF-SIMS imaging before and after the cleaning procedure noted that sulfuric acid effectively removed all observed contaminants, but the absence of the ^{6}Li signal after cleaning indicated that substantial Si was removed as well [7].

Method: The implanted surface of the Si wafer was etched (approximately uniformly) in the following way. Hydrofluoric acid was pre-diluted with nitric acid to a HF concentration of 1%. From this premix a 100 µL drop was placed in a clean Savillex™ PFA vial and the Si wafer placed on top of it, solar wind-exposed surface down, in order to dissolve the implanted solar wind with minimal Si-removal from the wafer. After 5 minutes the reaction was stopped by adding 900 µL water, the wafer was removed and the solution split in aliquots for isotope composition (IC) and isotope dilution (ID) measurements. As a spike for ID measurements, a well-characterized high-purity standard Lithium solution was used with a ^{7}Li/^{6}Li ratio of 15.1 ±0.3. The IAEA's L-SVEC natural Li standard was used to monitor instrumental mass bias. The partial dissolution was set up to dissolve ~300 nm per dissolution step (sufficient to remove the implanted solar wind). Each Si wafer was subjected to two dissolution steps to ensure that there was no ^{6}Li remaining in the Si wafer.

The aqua regia cleaning applied to 60491 and 60500 involved three steps, each of which was dried down and redissolved in 1 mL of 2% HNO_3 for ICP-MS measurements.

The measurements were performed on an Element XR™ at the Plasma Analytical Facility of the National High Magnetic Field Laboratory using Thermo Super Jet 8.2 Ni sampler and Spectron T1001 Ni-X skimmer cones with a sensitivity of 60 Mcps/ppb of ^{115}In. Sample introduction was performed with an ESI ApexQ™ sample introduction system and a 20 µL/min Savillex™ PFA nebulizer. The detection limit of ^{6}Li was 0.1 ppt or 0.00006E14 atoms ^{6}Li for 1 cm^2 wafer.

Discussion: The ^{6}Li fluence in the ion implantation at Kroko has been measured here by isotope dilution as 3.20E14 atoms/cm^2 (Table 1). This corresponds well with the nominal fluence provided by Kroko of 3E14 atoms/cm^2.

The ToF-SIMS study [7] showed that the aqua regia treatment produced surfaces from which most of the original particulate contamination had been removed. Measurements of the aqua regia cleaning steps on 60491 and 60500 showed no detectable ^{6}Li in the case of 60491 ($\leq$ 0.01% of total ^{6}Li based on 3E14 atoms/cc) and approximately 0.1% ^{6}Li in the case of 60500 (Table 1). Integrating the Mg profile that corresponds to the ^{6}Li profile, with the achievable precision of 1-2 ‰ in δ^{26}Mg, a shift in δ^{x}Mg is only resolvable for losses in ^{6}Li greater than 3%. Thus, the aqua regia cleaning procedure is aggressive on particulates originating from the crash, but does not measurably impact the underlying Si wafer.

Due to the high boiling point of sulfuric acid (330°C) it is not possible to dry down the acid, and the sulfuric acid cannot be directly introduced into the ICP-MS to measure the ^{6}Li removed during the cleaning step. So, no data is reported for this step in Table 1. ToF-SIMS images concluded that the sulfuric acid cleaning destroyed the solar wind layer in 60493 [7]. Sample 60493 was subjected to two HF-HNO$_3$ dissolution steps. The ^{6}Li implant recovered in the first step corresponds to <1% of the original implant. No further ^{6}Li was recovered in the subsequent dissolution step. This confirms the result of the ToF-SIMS analysis: boiling sulfuric acid cleaning of *Genesis* flight Si wafers destroyed the solar wind layer, although similar damage to non-flight controls was not noted.

Table 1: ^{6}Li recovery in cleaning and dissolution steps

Sample	Acid Cleaning	^{6}Li in acid cleaning step [E14 atoms\cc]	^{6}Li in HF-HNO$_3$ dissolution step [E14 atoms\cc]
Kroko			~3
A-5			3.20±0.28
60491	AR^a	0.0097	3.2
60493	SA^b	-	0.04
60500	AR^a	0.0026	2.7

^{a} *aqua regia*
^{b} *sulfuric acid*

HF-HNO$_3$ dissolution on sample 60491 and 60500 showed a full recovery of the ^{6}Li implant in the first dissolution step (Table 1). A second HF-HNO$_3$ dissolution performed did not yield any detectable ^{6}Li.

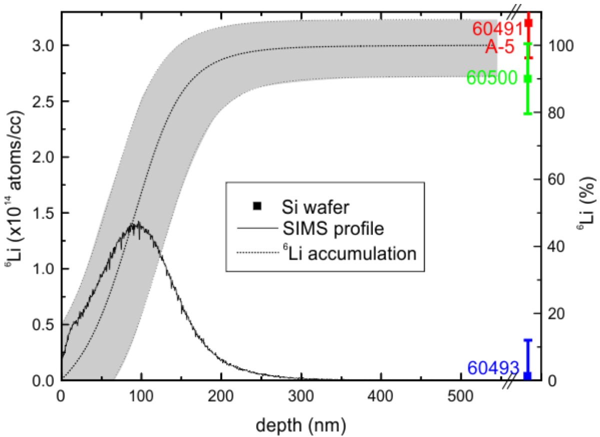

Figure 1: The cumulative ^{6}Li with depth from the surface is calculated from a SIMS depth profile and plotted as a black dashed line. The SIMS ^{6}Li profile is shown as a solid black line. The gray area represent a 10% error on the cumulative ^{6}Li. Sample and control measurements are represented by colored symbols. Note that the red square represents both the control A-5 and 60491.

The recovered ^{6}Li from 60491 and 60500 matches the expected fluence of 3E14 (± 10%) atoms/cc established by A-5 CZ within error. The fluence of the control A-5 and 60491 give exactly the same value. Sample 60500 is ~10% lower than the expected fluence; this is the sample where a pre-implant photograph of the sample plate shows conducting paint splashed on the surface prior to the implant process.

Conclusion: The aqua regia cleaning technique was found to not remove any significant ^{6}Li (<0.1%) from the implanted wafers. The HF-HNO$_3$ dissolution step obtained quantitative yields for ^{6}Li on each wafer. Each wafer was processed twice with HF-HNO$_3$ dissolution. The first dissolution step removed all of the ^{6}Li as expected, and no ^{6}Li was detected in the second dissolution step. We infer that we removed >300 nm of Si during each dissolution. These results demonstrate that – with a single ^{6}Li implant at 15 keV – Genesis Si collectors can be suitably used for Mg isotope analyses of the solar wind by ICP-MS analysis.

References:

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