MEASURING THE Mg FLUENCE OF THE SOLAR WIND USING LA-ICP-MS DEPTH PROFILING J. B. Wimpenny[1], Q.-Z. Yin[1], D. S. Burnett[2], A. J. G. Jurewicz[3], D. S. Woolum[4]. [1]University of California, Davis, CA 95616. Email: jbwimpenny@ucdavis.edu, qyin@ucdavis.edu [2]California Institute of Technology, Pasadena, CA 91125. [3]Arizona State University, Tempe AZ 85287. [4]California State University, Fullerton, CA 92831.

Introduction: The goal of the Genesis mission was sampling of the solar wind, from which to infer the composition of the solar nebula leading to our solar system. Recently, a growing number of studies have attempted to measure both isotopic compositions [1,2], and elemental fluences [3] from returned Genesis samples, to characterize the solar wind. Such analyses are complicated by the fact that the flux of material implanted by the solar wind is very small (2×10^{12} atoms of Mg per cm^2), and that the samples have been contaminated by terrestrial material when the spacecraft crash-landed on Earth. Hence any methods used to study the Genesis samples must be very sensitive, and must be able to account for contamination without affecting the implanted solar material at depth of only 100 nm from the sample surface.

So far, much of the work has been performed using SIMS [2] or RIMS [4]; while such work has excellent sensitivity for many elements, quantification is difficult, and corroborating analyses by different techniques will be important. Other elements, such as Ni and P, are difficult to measure by SIMS. In contrast, ICP-MS instruments scan quickly through the entire periodic table from Li to U producing quantifiable data and have comparable sensitivities for different elements. If it can be shown that easily available ICP-MS instrumentation can glean useful information from the Genesis samples, it gives us the potential to considerably speed up analyses of these precious samples.

One attempt to utilize ICP-MS has been to sequentially leach the silicon wafer [1], and then measure the composition of the leachate in solution. Such a technique gives a 'one shot' analysis, providing no information about the penetration depth of the solar wind implant. More importantly, satisfactory chemical leaching techniques to remove terrestrial surface contaminants are not yet available. Instead, in this study, we attempt to use ICP-MS to measure Genesis solar wind by introducing the sample as an aerosol using laser ablation. This has the advantage of being able to sample through the silicon, sapphire or any suitable target wafer materials through laser pulses, layer by layer, at controlled ablation rate. The data acquisition time is very fast (typically a minute or so per spot). No sample preparation is needed. A low-energy laser-pulse cleaning step can remove thin film contamination. An excellent optical viewing system can be used to avoid large particles. The presence of a submicron particle in the analysis spot can be recognized by a distortion in the depth profile or by an anomalously high fluence: with rapid data acquisition on a small spot, statistical sorting of the data is feasible.

We present ICP-MS Mg fluence data from silicon collectors with results similar to those attained using SIMS. In addition we show that laser systems can couple well with sapphire (hitherto unused target material on the spacecraft to collect solar wind) and suggest that our technique can also be applied to Fe and other elements when the background levels is reduced.

Methods: Laser ablation analyses were performed at UC Davis using a 193nm excimer laser (Photon Machines *Analyte 193H*) with the dual volume Helex sample cell -- designed to improve response time, and reduce spatial fractionation within the cell -- in combination with a high resolution ICP-MS (Thermo Fisher *Element XR*). To enhance the sample signal, the *Element XR* was fitted with a high sensitivity X skimmer cone, and Jet sampler cone. In addition, all sample tubes from the laser to the *Element* were new and flushed with He gas for extend period of time, to remove as much background as possible before analyses. Running the plasma overnight with the laser off resulted in significant background reduction.

Laser running parameters were chosen to ablate slowly through the sample, yet still producing enough signals above background. As such, analyses were performed using the largest spot sizes (85µm) and a laser energy of 5mJ attenuated to 10% power. The pulse rate is limited by the laser software; the lowest frequency being 1Hz. The laser gas flows were tuned for maximum sensitivity by measuring the ^{24}Mg intensity in NIST 612 glass: this also allowed us to estimate sensitivity of our system in cps/(atom/cc). The analysis routine involved rapid measurement of the three isotopes of Mg (^{24}Mg, ^{25}Mg and ^{26}Mg) along with ^{27}Al. Such rapid analyses allowed ~8 sample measurements to be made per laser pulse. Background levels were measured in a 10 second gas blank (i.e. laser off) prior to ablation. Background is entirely from the plasma source and mass spectrometer. Typical ^{24}Mg blanks were ~100-120 cps. The fast sampling rate generated a great deal of data. Due to low intensities of the signal, noise level needs to be reduced. This was done by subtracting the background and then binning data into more manageable packets; either into average counts per pulse, or the average over 100 data points.

Ablation pits were characterized by three independent methods; AFM (atomic force microscopy) at UC

Davis, a profilometer at ASU, and by laser interferometry at CalTech. Figs. 1 and 2 show examples of pit shapes in silicon, and sapphire, as imaged by AFM. Note the cleanness inside the laser crater seen in Fig. 1 (left panel) compared to the surrounding debris, demonstrating our technique can effectively remove small terrestrial contamination particles, which are notoriously difficult to remove mechanically or chemically.

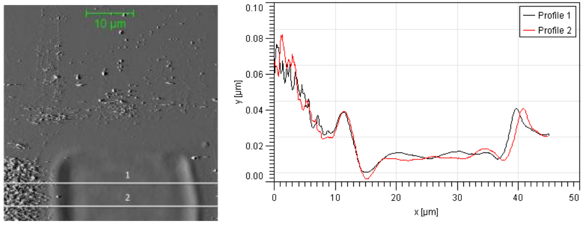

Fig 1. AFM analyses of a single laser ablation pit (30×30µm square, top half is shown) of a flight spare silicon CZ (Czochralski-grown) wafer at 10% laser power attenuation. Average crater depth is ~10 nm/pulse. The raised release at the edge is inferred to be ablation debris.

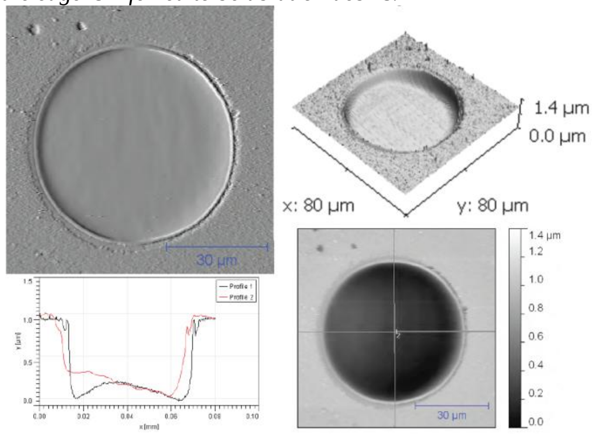

Fig. 2 An example of AFM analysis of ablation pit on sapphire flight spare. 50 pulses give a pit depth of ~800nm, or ~15nm per pulse.

Results and Discussion: Analyses of the implanted wafer (Fig. 3) show that the implanted Mg can easily be measured by laser ablation. The laser energy couples well with the silicon metal and sapphire. The first pulse (Fig. 3) samples primarily surface contamination. The majority of the implant ^{25}Mg occurs in subsequent pulses. A single pre ablation pulse may be sufficient to clean any terrestrial debris from the flight sample. A previous measurement of the Mg fluence in the solar wind by SIMS gave a value of 2.02×10^{12} atoms/cm^2 [3]. We performed 4 depth profiles through the Genesis flight sample (Fig. 4) by laser ablation and attained a range of Mg fluences from 2.15 to 2.40×10^{12} atoms/cm^2 in three of these profiles. The first profile measured gave a slightly lower value of 1.36×10^{12}. The measurements were made with ^{24}Mg. ^{25}Mg and ^{26}Mg signals were too low (within error of background, thus at present this technique is not yet able to give an isotopic ratio.

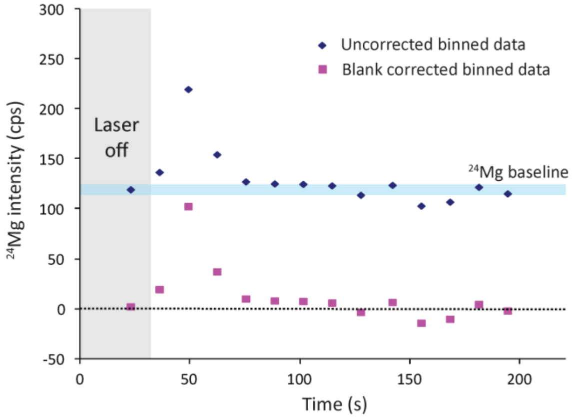

Fig. 3 – Measured ^{25}Mg intensity through an implanted silicon wafer. The number of pulses can be translated into depth through the sample by the average depth per laser pulse (e.g. ~10nm/pulse).

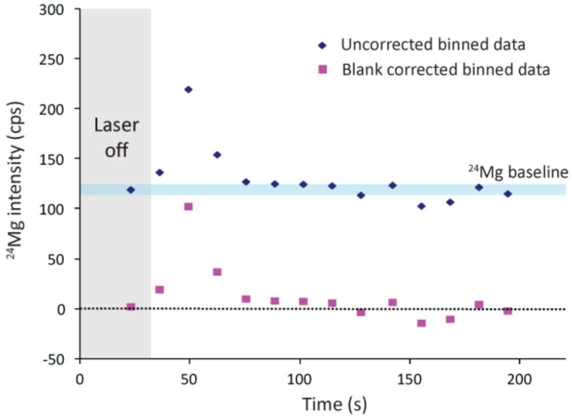

Fig. 4 – Profile showing the ^{24}Mg intensity measured in a Genesis flight sample. Data points represent bins of 100 measurements with the majority of Mg present within the first 20 pulses.

Clearly, these results show that there is great potential in using laser ablation to measure the fluence of Mg in these samples. Not only that, but further testing has shown that the laser energy couples well with sapphire (Fig 2), and that blank levels in our system are sufficiently low enough for us to measure Fe. Ni and other elements if we use Pt tipped cones. Future work will also involve testing materials used in the concentrator (with an order of magnitude higher implanted material). This material may allow us to analyse Mg isotopes as well as some elements thought to be out of range due to high backgrounds

References: [1] Humayun et al. (2011) 42nd LPSC, A.1211. [2] Heber et al (2011) 74th MetSoc, A.5510. [3] Jurewicz et al. (2011) 42nd LPSC, A.1917. [4] Veryovkin et al. (2011) 42nd LPSC, A.2308.