RIMS ANALYSIS OF SOLAR WIND MAGNESIUM AND CALCIUM IN GENESIS SAMPLES. * I. V. Veryovkin[1], C. E. Tripa[1], A. V. Zinovev[1], J. M. Hiller[1], M .J. Pellin[1], and D. S. Burnett[2] [1] Materials Science Division, Argonne National Laboratory, 9700 S. Cass Ave., Argonne, IL 60439 (email: verigo@anl.gov), [2] Division of Geological and Planetary Sciences, Mail Code 100-23, California Institute of Technology, Pasadena, CA. 91125.

The Genesis Discovery mission has delivered samples of the solar wind (SW) for analysis of isotopic and elemental compositions using the most advanced analytical techniques available in laboratories on Earth. The terrestrial contamination, which occurred during the crash landing of the Genesis sample return capsule, has made accurate analyses of these samples of solar matter very difficult and thus facilitated further improvement of analytical instruments and development of many new analytical procedures. Under these circumstances, Resonance Ionization Mass Spectrometry (RIMS) based on ion sputtering of a sample surface and laser post-ionization of the sputtered neutral atoms has proved to be a sensitive, accurate and robust analytical method well suited for the quantitative analysis of the Genesis SW collectors. At Argonne National Laboratory, we are conducting RIMS analyses of these collectors using a novel time-of-flight mass spectrometer, SARISA, which was specifically developed and optimized for this kind of measurements [1]. In the focus of our work on the Genesis samples are various metallic elements whose SW concentrations range from above one part per million ($>10^{-6}$) to below one part per trillion ($<10^{-12}$) [2].

Magnesium was selected as the first SW element for RIMS analysis. Its relatively high abundance in the SW (estimated 2-year fluence of 2×10^{12} at/cm^2 [2]) made it suitable for testing and improving RIMS instrumentation and experimental procedures in order to achieve the best accuracy and precision of the method. We made preliminary measurements of abundances of Mg in two types of SW collectors, silicon and diamond-like carbon (film on silicon). These were sputter depth profiling experiments conducted in Resonance-Enhanced Multi-Photon Ionization (REMPI) regime, in two-color scheme with two Ti-sapphire post-ionization lasers tuned to 285.296 nm and 375.66 nm wavelengths, at a repetition rate of 1 kHz. In order to make our measurements quantitative, we used two specially prepared standard reference samples, made from exactly the same materials as the flown Genesis collectors and implanted with a known fluence of 43 keV Mg ions: 2×10^{13} at/cm^2 in dia-mond-like carbon and 1.1×10^{13} at/cm^2 in silicon. The ^{25}Mg isotope was significantly enhanced in these reference samples in order to help to distinguish the implant from any terrestrial surface contamination (where ^{24}Mg has the highest abundance). These measurements allowed us to characterize the actual efficiency and detection limits of the new SARISA instru-ment: the useful yield of the instrument peaked at about 20% with a mass resolution of ~2000 and detection limits corresponded to < 50 parts per trillion.

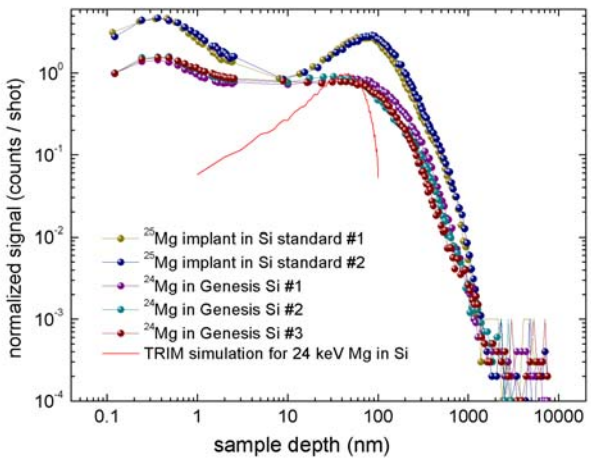

Figure 1 Depth profiles of SW Mg in Si compared to the Mg implant standard reference material

We measured concentration vs depth profiles for Mg in solar wind collectors (Si and diamond-like carbon, respectively) and compared them to Mg implant standards. One apparent feature of the solar wind implants was that the maxima of these profiles were broad, with an apparent diffusion of the implanted atoms towards the surface (Fig.1). Since the Genesis solar wind collectors were subjected in space to intense bombardment by protons and alfa-particles, and solar light heated them to the temperature of ~200 °C for nearly 2 years, one can explain this feature as an effect and consequence of radiation-enhanced thermal diffusion processes. The total fluences of Mg in solar wind determined from our measurements were: $(2.74\pm0.20)\times10^{12}$ and $(2.46\pm0.20)\times10^{12}$ at/cm^2 for Si and diamond-like carbon collectors, respectively (at 2σ error level) [3].

To further improve the accuracy and sensitivity of our RIMS measurements, we introduced several important modifications in our instrumentation and analytical procedures, as follows. First, we modified the operation regime of the SARISA instrument so that experiments can be conducted at 2 kHz repetition rate instead of the previously used 1 kHz. We introduced an interleaved regime of data acquisition, such that RIMS data acquisition can be performed at 1 kHz rep rate and be interleaved with another 1 kHz data acquisition process dedicated to non-RIMS background. For our sputter depth profiling measurements, this ×2 accelerated instrument operation mode produces much more experimental data during the same time. This translates into an improved precision of the non-RIMS background measurements and the overall accuracy of the acquired data. Second, a new measurement procedure utilizing a secondary glass (bulk) standard calibrated by us against the primary implant standard was introduced in order to shorten the measurement time and thus to minimize and to better account for the effects of any long-term instrumental drifts. To perform reproducible RIMS analyses with these secondary standards, we have equipped the SARISA instrument with the electron flood gun for sample charge compensation. As a part of this mitigation of instrumental drift dependences, we also introduced thermal stabilization into certain critical components of our RIMS lasers. Third, we are presently testing back-side depth profling as an alternative method, which should allow us to minimize the influence of the sample surface contamination. All these improvements aim at producing a set of RIMS data on elemental abundances in solar wind with the best achievable accuracy and precision to-date. We are presently completing these Mg RIMS measurements that take advantage of the mentioned above improvements.

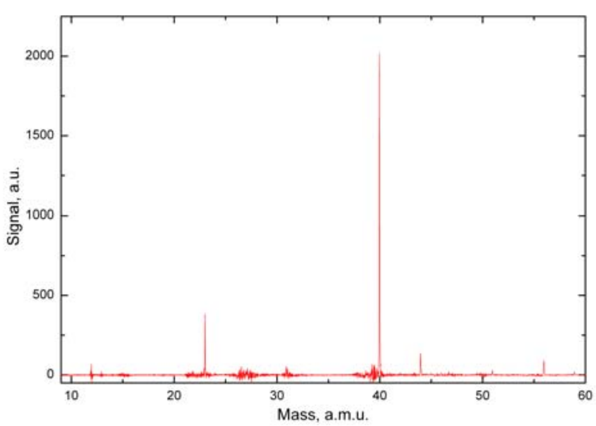

Figure 2 RIMS spectra of Ca from glass standard reference material. ^{40}Ca peak is clearly seen. REMPI with one tunable Ti-sapphire laser: fundamental radiation with 719.568 nm (1.72 eV photon) is used for the ionization step, and the 3rd harmonic radiation with 239.856 nm (5.17 eV photon) is used for resonant excitation from groundstate to intermediate state.

We are also conducting preliminary measuments of elemental abundances of Ca in Si SW collectors. Presently we are evaluating various REMPI schemes for Ca. Figure 2 shows Ca photoions measured on the NIST SRM-611 glass standard by one of the tested REMPI schemes. In particular, we are looking for a laser ionization scheme that would allow us to simultaneously measure Ca and Al in Genesis samples. This can be done using a similar approach to that used for Ca and outlined in the caption to Fig.2. For example, the resonant transitiona for both elements can be chosen such that they are very similar (e.g. 272.165 nm for Ca and 265.248 nm for Al), corresponding to the 3rd harmonics of two tunable lasers. The residual 2nd harmonic radiation from both tunable lasers can then be used to ionize both elements simultaneously.

Ca and Al are not only relatively abundant SW elements, with concentations only about an order of magnitude less that for Mg, but they are also interesting for cosmochemistry. Ca-Al-rich inclusions (CAIs) [4] found in carbonaceous chondrites have been a rich source of isotopic anomalies that are thought to reflect much larger degrees of physical mass fractionation effects than are present in terrestrial materials. It would be interesting to determine what is the Ca/Al ratio in the solar wind [5, 6]. According to estimates from [1], it is expected to be between 0.717 and 0.75.

At the conference, we will present our best results on Mg and also preliminary results on Ca.

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