THE CHALLENGE OF MEASURING ULTRA-LOW ELEMENTAL ABUNDANCES IN GENESIS SOLAR WIND COLLECTORS.

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Introduction: Aiming at accurate determination of the original ingredients in the solar nebula and better understanding of how this nebula evolved into our Solar system, the Genesis Discovery mission collected samples of solar wind (SW) and returned them to Earth for quantitative isotopic and elemental analyses [1, 2]. To date, the main mission objectives have been successfully met [2] despite performing analyses for Genesis SW collectors was a very difficult task. The difficulties arose from the fact that the SW matter is implanted at very shallow (<100 nm) depths under the collectors surface, which was contaminated both by the exposure to outgassing spacecraft materials and by the hard impact landing of the Genesis sample return capsule. One of the specific mission measurement objectives remaining to be met is the analysis of elements in the mass range 80-100. Using different subsets of these SW elements, two major cosmochemical issues can be addressed: (a) the gas-dust fractionation in solar accretion process via comparison of the volatile Kr with non-volatile Se, Rb and Sr, as proposed in Ref. [3], and (b) the elemental abundance distribution structure in the N=50 closed shell region with Sr, Y and Zr. These elements are implanted in the Genesis SW collectors fluences between ~ 8.8×10^6 at/cm^2 (Y) and 1.2×10^8 at/cm^2 (Se) [1], which is two to three orders of magnitude lower than the lowest fluences measured in the Genesis SW collectors by SIMS and RIMS techniques [2, 4]. In this work, we discuss the challenge of measuring such ultra-low elemental fluences and describe the strategy allowing us to take on this challenge.

The limited number of SW atoms in the analysis spot is the root cause of this challenge. From Fig.1, one can see that an analytical probe 100 µm in diameter would "see" only ~10^4 Se and <10^3 Y atoms. In this case, SIMS with typical ion yields <10^{-2} would be able to detect less than 100 Se or 10 Y ions in total. Moreover, even with no background noise taken into account, these ion numbers would be further scaled down by (1) instrumental transmission and (2) detection efficiency. For commercially available SIMS instruments, achieving the required elemental accuracy of $2\sigma=10\%$ for these SW elements is a grand challenge because it requires analysis of large (sub-mm) spots using low energy primary ions. This results in prolonged analysis time (hours per spot) with extremely low rates of ion count per sec. For RIMS, the situation is not much easier. For example, with the "spot-hammering" RIMS analysis method [4], which is op-
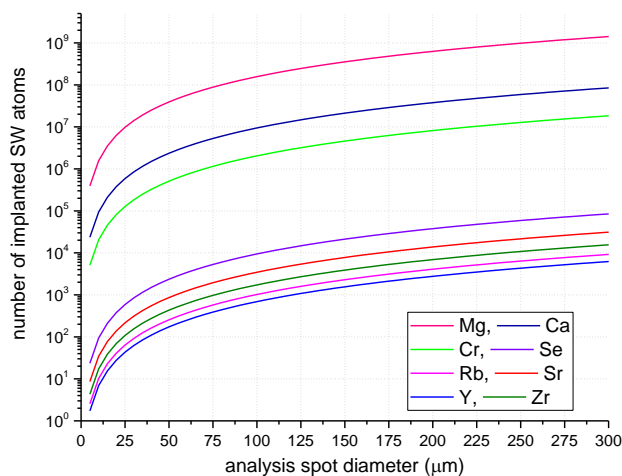

Figure 1. Number of SW atoms available in the analysis probe spot calculated from estimates of SW fluences provided in Ref.[1].

timized for maximum efficiency of photo-ion detection, each such analysis spot would require about 2 hrs of pulsed ion bombardment, using ~7×10^6, 10 keV primary Ar$^+$ ions (500 ns pulses @ 400 nA ion current with 1 kHz repetition rate) and producing ion count rates *less* than 1.4×10^{-4} photo-ions per analysis shot. In this case, *how much less* depends on the useful yield of the RIMS instrument, which is a product of: (1) instrumental transmission, (2) detection efficiency, (3) photo-ionization efficiency, and (4) total fraction of volatilized neutral atoms intercepted by the laser beam. While factors (1) and (2) are the same in nature as in SIMS, the factors (3) and (4) are laser-specific. The conditions of RIMS analysis can improve if ion sputtering is replaced with laser ablation. In this case, millions of primary ion pulses can be replaced by a few tens of laser ablation shots, thus dramatically improving the ion counting statistics and shortening analysis times. *In our opinion, for successful RIMS analyses of Se, Rb, Sr, Y and Zr in Genesis SW collectors using the laser ablation probe instead of the ion beam is a must.* For most accurate sample material volatilization, the ablating laser should generate femtosecond pulses and its beam profile should be homogenized to have flat-top shape (aka "top-hat"). This enables RIMS in laser ablation "spot hammering" regime, with depth resolution of a few nm per laser shot so that the entire spot can be sampled by a less than a hundred laser shots.

We developed a special physical model to better understand the dynamics of the process determining the factor (4) named above. Fig. 2 shows physical lim-
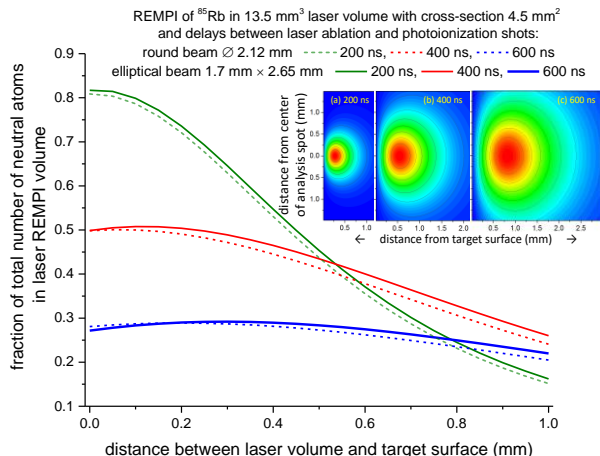
Figure 2. Fraction of neutral atoms intercepted by photo-ionizing laser firing with delays of 200 ns, 400 ns and 600 ns after the end of the volatilization pulse (in this case, laser ablation). Insert: spatial expansion of the plume of volatilized neutral atoms.

its of the useful yield of RIMS, which we determined with this model. For example, if factors (1)-(3) above are set to unity (i.e. perfect transmission, detection and ionization efficiency), the useful yield with large photo-ionization volumes of 13.5 mm^3 cannot exceed 80% when this volumes starts right at the sample surface. Fig. 3 shows the dependence of elemental accuracy 2σ on the analytical spot size for more realistic experimental conditions (0.5 mm distance from the surface and the combined product of $(1)\times(2)\times(3)\approx0.5$ to produce useful yield of ~20%). One can see that with this useful yield of RIMS, sizes of analysis spots needed for achieving the required 10% accuracy become smaller than 100 µm. This is a clear indication of feasibility of such analyses. At the same time, Fig.3 reveals another challenge for these analyses: *the quantitation*. Higher abundance SW elements Mg, Ca and Cr are shown here (and in Fig.1) for a reason: in order to
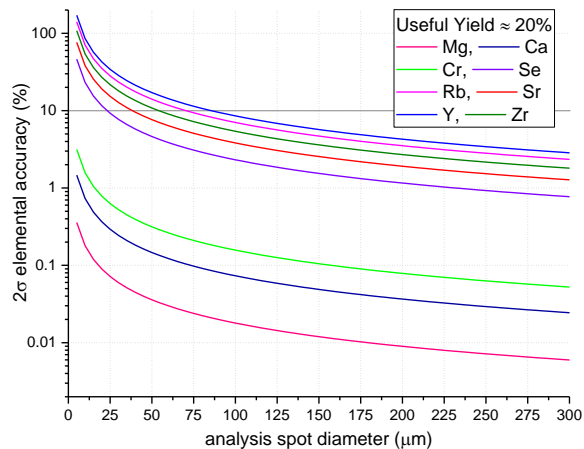

Figure 3. Elemental accuracy as a function of analytical spot size for RIMS with 20% useful yield.

quantitatively determine fluences of these elements, special standard reference materials (ion implants) with fluences $>10^{12}$ cm^{-2} had to be fabricated. These fluences are at the very edge of what could be independently quantified by other analytical techniques. If we use similar standard reference materials for laser ablation RIMS measurements of Se, Rb, Sr, Y and Zr, the detector will be easily overwhelmed by more than four orders of magnitude higher numbers of photo-ions per analysis shot.

Fortunately, we have developed an instrumental solution for this problem, called the Right Angle Ion Mirror-Prism, *RAIMP* [5]. This is a novel time-of-flight mass analyzer (Fig.4) featuring a special adjustable slit, which can be used to efficiently control the energy range of ions reaching the detector and thus filter out all (or most) secondary ions (i.e. noise counts). This dramatically improves signal-to-noise ratio of
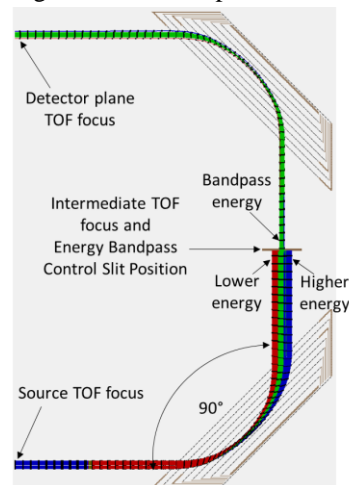

Figure 4. RAIMP combines two electrostatic mirrors with an energy bandpass control slit. This creates a unique synergy between two techniques: slit spectroscopy and time-of-flight mass spectrometry.

RIMS analyses. Moreover, this slit can also be used to attenuate the signals of photo-ions and protect the detector from being overwhelmed when we measure the standards with high elemental fluences. Importantly, this calibrated attenuation does not affect experimental conditions of RIMS, so that *SW samples can be done exactly in the same way as the standards*. The prototype of RAIMP was fabricated at UIC, and its experimental tests in RIMS analyses with start soon.

At the conference, we will present the RAIMP concept and discuss how it allows us to take on the challenge of quantitative RIMS analyses of elements with ultra-low abundances in Genesis SW collectors.

References: [1] Burnett D. S. et al. (2003) *Space Sci. Rev. 105,* 509–534 [2] Burnett D. S. and Genesis Science Team (2011) *PNAS 108* (48), 19147-19151. [3] Wiens R. et al. (1991) *Geophys. Res. Lett. 18* (2), 207–210 [4] Veryovkin I. V. et al. (2014) *LPSC XXXXV*, Abstract #2795. [5] Veryovkin I. V. and Hanley L., (2017) *Proc. 65th ASMS Conf. Mass Spectrom. and Allied Topics*, Citation ID 288660 / ThP 373