

# Measuring the Isotopic Composition of Solar Wind Noble Gases

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## 1. Introduction

It is generally accepted that the primitive Sun, which contains the vast majority of the mass of the solar system, has the same composition as the primitive solar nebula, and that the contemporary Sun has a similar composition except perhaps for light elements modified in main sequence hydrogen burning. The diversity of isotopic and elemental compositions now observed in various solar system reservoirs is most likely the result of subsequent modification and noble gases can provide us with valuable tools to understand the evolutionary paths leading to these different compositions. However, to do this we need to know the composition of the Sun with sufficient precision to delineate the different paths and processes leading to the variations observed and how the present solar wind noble gases may differ from that composition.

Solar optical spectroscopy, the main source of early knowledge about composition of the Sun, does not reveal isotopic information and noble gases do not have useful lines in the solar spectra except for He which was, interestingly, first found in the Sun by this method. Early estimations of solar abundances were based on the combination of photospheric spectral data and laboratory analysis of primitive meteorites which carry a clear signature of their original noble gases. This approach is justified by the fact that the CI chondrites, a rare class of primitive meteorites, and photospheric spectroscopy yield almost identical abundances of most nonvolatile elements. Since meteorites, which were formed by the preferential accretion of solids, clearly differ from the unfractionated solar nebula, the composition of primitive meteorites does not provide a suitable measure of solar system volatiles. Noble gases in meteorites are depleted by many orders of magnitude compared with the solar nebula and, although lunar soils and breccias, implanted with solar wind noble gases, did provide a needed ground truth, neither by themselves could provide a good values for solar volatiles. The first “best estimate” of solar abundances was found by interpolating between adjacent non-volatile elements (Anders & Grevesse, 1989), supplemented with the lunar data, and the later updates (Palme and Beer 1993, Grevesse & Sauval 1998, Lodders, 2010) provided presumably more reliable estimates, but all failed to supply precise isotopic, or even elemental, compositions of the solar noble gases.

Light solar wind noble gases were directly measured by mass spectrometers on various spacecrafts. The most recent of those missions were WIND, Ulysses, SOHO (Solar and Heliospheric Observatory) and ACE (Advanced Composition Explorer), see NASA website and review papers (i.e. Wimmer-Schweingruber, 1999, 2001). But the flux is low for the heavier noble gases, and the compositions of the light gases are known to vary with energy, so none of these provided solar isotopic and elemental abundances with sufficient precision.

The Apollo and Luna missions delivered samples of solar wind (SW) accumulated over million years in the lunar regolith. Besides the shallowly implanted SW noble gases, these samples also contained deeper noble gases mainly produced by the spallation reactions of cosmic ray protons and secondary particles, and compositions may be modified by diffusion. In order to delineate the various components, these gases were extracted using stepped pyrolysis and analyzed in sensitive mass spectrometers operated in the static mode. At low temperatures the released gases were dominated by “surface-correlated”, mostly SW, while at high temperatures they were mainly “volume-correlated”, mostly spallation-produced, noble gases and other in-situ contributions such as radioactive decay. To determine SW compositions, isotope correlation analyses were used. In three-isotope correlation plots two component mixtures are distributed in linear arrays, while for three component mixtures the data fill two-dimensional figures whose apexes define the pure end-member compositions. Several independent analyses using slightly different databases, slightly different techniques and somewhat different assumptions yielded several slightly different compositions for the heavy solar noble gases Xe and Kr. These compositions are referred to as BEOC 10084 (Eberhardt et al., 1970), SUCOR (Podosek et al., 1971) and BEOC 12001 (Eberhardt et al., 1972). Later, in attempts to better separate SW and gases that resided more deeply, stepped extractions from grain-size separates of the lunar fines were carried out (Drozd et al, 1972; Behrmann, et al, 1973; Basford et al., 1973; Bernatowicz et al., 1979) and a lunar soil 71501 was studied using in-vacuo stepped-etching technique (Wieler & Baur., 1995). This technique called CSSE (for Closed System Stepped Etching) allowed a better depth resolution of SW noble gases while reducing the potential mass-fractionation during stepped pyrolysis. Beside lunar soils (Wieler et al., 1986), SW-rich meteorites (e.g. Pesyanoe) were studied and, after significant spallation and other corrections, these studies yielded yet another composition for heavy noble gases in the solar wind (Pepin et al., 1995). All of these determinations of SW noble gases were in general agreement but there were slight differences in composition and no general consensus as to which was best.

One of the major complications was the presence of two seemingly distinct SW noble gas components, apparently residing at different depths within a given target: the “normal” SW and the more deeply implanted, presumably the more energetic component, subsequently labeled SEP, for the Solar Energetic Particle component (not to be confused with SEP, a label for solar flares by the solar physics community). The SEP “component” was first identified by Black & Pepin (1969) and Black (1972) with an apparent  $^{20}\text{Ne}/^{22}\text{Ne}$  ratio  $<11$ , much smaller than “normal” SW value of  $^{20}\text{Ne}/^{22}\text{Ne} = 13.7 \pm 0.3$ , and they then called it Ne-C or Ne-SF assuming that it was produced by Solar Flares. The low  $^{20}\text{Ne}/^{22}\text{Ne}$  ratio was supported by direct Ne analyses in solar flares (Dietrich & Simpson, 1979, Mewaldt et al., 1981, 1984), so this interpretation gained even more supporters (i.e. Nautiyal et al., 1981, 1986, Benkert et al., 1993) but it had to be much lower in energy than these solar flares. Wieler et al (1986) suggested replacing the term SF with SEP (for Solar Energetic Particles) since the SEP must have energies intermediate between SW and SF ions, and because the SF

flux was insufficient to produce the quantity of SEP observed. The proposed SEP component was assumed to have more energy than the typical SW of  $\sim 1$  keV/nucleon but far less energy than the solar flares ( $\sim 1$  MeV/nucleon), commonly referred to as SEP particles by the space physics community, so this terminology was confusing.

There were still more problems in interpreting noble gases released from lunar soils, lunar breccias, and gas-rich meteorites even though they were dominated by the solar wind. Radiation damage and disruption caused by solar wind hydrogen in surfaces exposed to the SW for as little as tens of years leads to lattice defects, enhanced diffusive losses and accelerated surface erosion (compared with laboratory simulations on undamaged samples). With enhanced diffusive losses comes an exaggerated isotopic fractionation effect. The Apollo Solar Wind Composition (SWC) experiment was designed to measure the light solar wind noble gases on pristine metallic surfaces without such effects, and it was successfully carried out during Apollo 11-16, the first five lunar landing missions. In this experiment the Apollo crews exposed Al- and Pt-foils to the SW for up to 45 hours and the foils were returned to Earth where the directly implanted SW-He, Ne and Ar were analyzed in noble gas mass spectrometers (Geiss et al., 1972, 2004). Since the exposure was short enough to avoid saturation effects, it was too short for analyses of the least abundant Xe and Kr and even the Ar analysis ( $^{36}\text{Ar}/^{38}\text{Ar} = 5.4 \pm 0.3$ ) was not sufficiently precise to delineate solar from terrestrial argon. Moreover, the light noble gases implanted in the foils were easily contaminated by small amounts of dust from the lunar regolith which contained large concentrations of noble gases implanted in the dust by the solar wind but altered by the processes just discussed. Although the dust was largely removed, and these foils represented the best solar wind data for the light noble gases at that time, the problem was not completely resolved.

The Genesis Space Mission (<http://genesismission.jpl.nasa.gov/>; Burnett et al, 2003) provided a dramatic improvement over the SWC experiment. With more than 400-times longer exposure, much purer collector materials, and free from contamination by most other components, it collected pure contemporary solar wind from outside of the terrestrial magnetosphere. Not only could the compositions of noble gases be determined with new precision, but many other elements could be measured as well including N and O. Ultrapure materials, prepared exclusively for the purpose of SW collection with low-blank analyses (Jurewicz et al., 2003), were exposed to the SW for 27 months at the L1 Lagrangian point, a pseudo-stable location which orbits with the Earth between the Sun and the Earth.

On September 8, 2004 the Genesis returned capsule landed although, due to a parachute failure (Genesis Mishap Investigation Report, 2005), it was not as "soft" as was originally planned. The "hard" landing caused significant delay in SW analyses because of the need to identify and clean several thousand fragments of broken collectors and, in many incidences, develop new techniques for the analyses. In spite of this, Genesis turned out to be a very successful mission with most of the original objectives met, in fact it was the first successful sample return mission since the Apollo era. We present here the results of a comprehensive analysis of SW noble gases collected by the Genesis SW-collectors. All of the analyses reported here were performed at Washington University in St. Louis using mass-spectrometers especially developed for Genesis and laser extraction techniques that continued to evolve during the course of analyses for the mission, descriptions of which are presented in this study.

## 2. Solar wind collection

Highly ionized solar wind ions,  $\sim 1\text{keV/nucleon}$  energy, can be effectively collected by most solids, penetrating the lattice, losing energy by scattering, and coming to rest at a depth (range) that is characteristic of the ion, its energy and the target material. Once an energetic ion penetrates a solid it becomes quickly stripped of all residual electrons. After it slows down sufficiently to pick up electrons from the lattice, its charge state is determined by its instantaneous energy and the composition of the target material. Each scattering outcome depends upon specific impact parameters and the interactions between the incident ions and the lattice electrons result in quantum exclusions of some otherwise available states. The constantly changing energy makes these effects even more complex so, in spite of long efforts of many renowned physicists (e.g. Fermi, 1940; Bohr, 1940; Knipp and Teller, 1941 and others), no analytical solution for the ranges of ions has been found. Instead, a Monte Carlo approach is commonly used to simulate each scattering, statistically tracking the trajectory and energy of a population of energetic ions penetrating solid materials and arriving at a distribution of expected ranges as a function of the ion, the initial energy and the target material.

SRIM (the **S**topping and **R**ange of **I**ons in **M**atter) is a suite of the computer codes which calculate the ranges of ions from  $10\text{ eV/nucleon}$  to  $2\text{ GeV/nucleon}$  in various materials based upon Monte Carlo simulations of successive scatterings, with intermediate trajectories and energies defining conditions for subsequent scatterings, leading to a final distribution of penetration depths (Ziegler et al., 2008, and available at [www.srim.org](http://www.srim.org)). Figure 1 displays SRIM-2008 results for normal incident solar wind noble gases stopping in aluminum. As can be seen, while heavy noble gases penetrate deeper than lighter ones, all implanted SW-noble gases reside within the outermost  $0.3\text{ }\mu\text{m}$ . Therefore, the active portion of the Genesis SW-collectors need not be thicker than a micron or so. Since such a thin foil cannot support itself

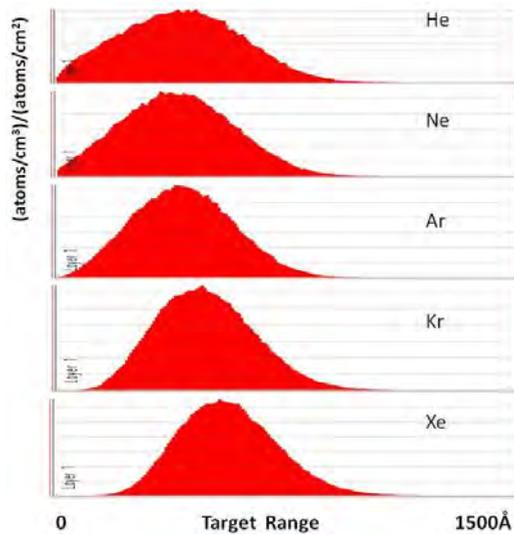


Fig. 1. Depth profiles of noble gases implanted into aluminum at  $1\text{keV/nucleon}$  energy. Calculated by SRIM-2008 (Ziegler et al., 2008).

or withstand spacecraft mechanical stress, Genesis collectors are made using an active layer of collector material  $\sim 1 \mu\text{m}$  thick deposited on sapphire substrate material (Jurewicz et al., 2003). These “sandwiches” turned out to be very convenient for laser extraction techniques because the laser energy is confined to the coatings where all implanted SW reside. Thus, there is no thermal coupling to the substrate so the substrate does not contribute to background effects from either indigenous or trapped atmospheric noble gases, both of which are ubiquitously present at various levels in all materials including the substrate material used here. This was another significant improvement of the Genesis SW collectors over those of the Apollo SWC experiment in which the foils were self-supporting aluminum films  $\sim 15 \mu\text{m}$  thick with the noble gases extracted by pyrolysis (complete melting) of the foils, resulting in noble gas backgrounds at least 15 times higher than in the Genesis 1- $\mu\text{m}$  ultrapure coatings on sapphire.

## 2.1 Aluminum solar wind collectors

Two types of SW-collectors were used in this study: AloS ( $\sim 15 \mu\text{m}$  Aluminum deposited on Sapphire substrates) and PAC (Polished Aluminum Collectors). The latter consisted of 0.05” thick highly polished T6 6061 Al-alloy, a material not intended to function as a SW collector but as a thermal control surface. After the hard landing the PAC turned out to be the largest area available for the analyses of SW noble gases, especially important for the heavy noble gases.

Prior to Genesis mission, we had developed a unique method for collecting low-energy cometary volatiles by growing low-Z metal films on sapphire substrates (Hohenberg et al., 1997). This method utilized a technique we referred to as “active capture” and involved the “anomalous adsorption” of Xe and Kr at chemically active sites, permanently entrapping them in the growing metal films (Hohenberg et al., 2002). Anomalous adsorption is a term we use to distinguish the chemical bonding of heavy noble gases from conventional Van der Waals adsorption and requires the availability of unfilled bonds. In the course of refining the active capture technique, low background laser ablation methods were developed to extract noble gases from these films, during which backgrounds, trapping efficiencies and other properties of these films were extensively studied. A natural extension of this work led to the optimized Genesis SW collectors and recovery techniques of impinged SW gases.

The aluminum on Sapphire (AloS) collectors have many advantages over other thin films and over the polished aluminum collectors (PAC). First, Al has a relatively low melting point compared to other metallic films, requiring less laser power for ablation and therefore less energy deposited in the laser extraction cell which results in lower noble gas backgrounds (blanks), especially important for the low abundance heavy noble gases. Second, the low-Z of the target aluminum means that the backscatter of SW ions will be much smaller compared with other potential collectors such as Au, requiring a much smaller back scatter correction especially for the light noble gases where the projectile Z is also low. Third, aluminum is a good conductor, eliminating any charging effects. Finally, the rapid diffusion of hydrogen in Al (compared with Si and other collector materials) reduces lattice damage and lattice distortion effects caused by the huge amounts of SW hydrogen which can adversely affect the quantitative retention of the light noble gases. Moreover, these SW hydrogen effects are difficult to properly model or simulate so reducing the problem is the best way to minimize the effect (Meshik et al., 2000).

The main disadvantage of AloS is that the Al coating is somewhat fragile and can be easily damaged. Several scratched fragments of AloS have demonstrated measurable SW-He

losses, especially for the light  $^3\text{He}$  isotope, making the remaining He isotopically heavier (Mabry, 2008).

The solid aluminum SW collector, PAC (Figure 2), is a harder material than the AlO<sub>3</sub> film, thus it is somewhat more robust, but the excellent thermal conduction properties of solid aluminum requires a UV laser to adequately couple to the aluminum and a short-pulse to deliver the energy faster than the energy dissipation from the laser pit (“explosive” degassing with each laser pulse). This places some constraints on the laser system but it also provides means for better depth profiling of the released gases.

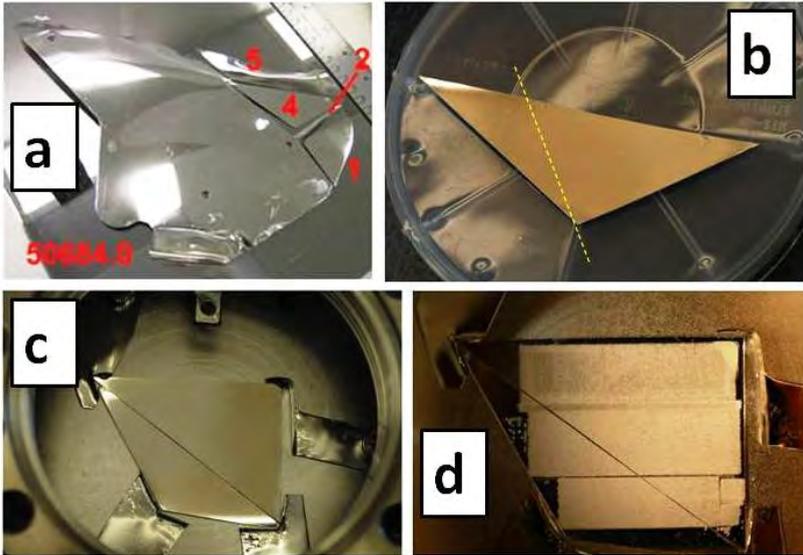


Fig. 2. Genesis Polished Aluminum Collector (PAC) cut in several fragments - (a). Fragment #4 was further split in two parts - (b), which were rearranged for UV-laser ablation and loaded into extraction cell - (c). Last panel (d) shows the PAC after analyses of noble gases released during the ablation.

### 3. Experimental

#### 3.1 Extraction of noble gases from Genesis solar wind collectors

There are several ways of extracting noble gases from Genesis SW-collectors. The first is simple pyrolysis, melting of the material carrying the SW and extracting noble gases in a single step from the melt. The second is step-wise pyrolysis, increasing the temperature incrementally in steps, allowing extraction by enhanced diffusion, first from the weakly bound sites, usually the shallowly implanted noble gases (and most of the superficial contamination), then progressively from the more deeply implanted noble gases. This method was extensively used in the analyses of SW implanted into lunar soils and breccias, SW-rich (referred to as gas-rich) meteorites and the Apollo SWC-experiments. The third technique, mentioned above as CSSE (Wieler & Baur, 1994), which, in contrast with step-wise pyrolysis, is a step-wise etching method. This is carried out at constant temperature,

allowing a better depth resolution of SW noble gases and eliminating some of the mass-fractionation caused by diffusion in step-wise pyrolysis. An elegant version of CSSE was developed for Genesis gold SW-collectors which were step-wise amalgamated *in vacuo* by mercury vapor, thus incrementally releasing SW gases. This technique was also used in analysis of Genesis AuoS (gold film on sapphire) and the solid gold foils (Pepin et al., 2011).

During the evolution of Genesis noble gas analyses, laser extraction techniques were further developed (Meshik et al., 2006) reducing the background even more for the PAC collectors. This provided an alternative to step-wise pyrolysis and CSSE. Gradually increasing the applied UV- laser power with each raster was thought to be capable of separating surface contamination from the more deeply implanted SW noble gases. However, there were considerable complications especially for the low abundant heavy noble gases which required the ablation of several square centimeters of the PAC SW collector to extract enough SW gases for precision measurements. During the process, sputtered aluminum from the collector was deposited both on the walls of the extraction cell and on the internal surface of the vacuum viewport, thus attenuating the laser power delivered to the sample while heating the viewport and the whole extraction cell. This progressively decreased the extraction efficiency of the laser and increased the noble gas background. During the course and evolution of these analyses several improvements were made which reduced the sputtering of collector material on the viewport (Figure 3) and the associated viewport

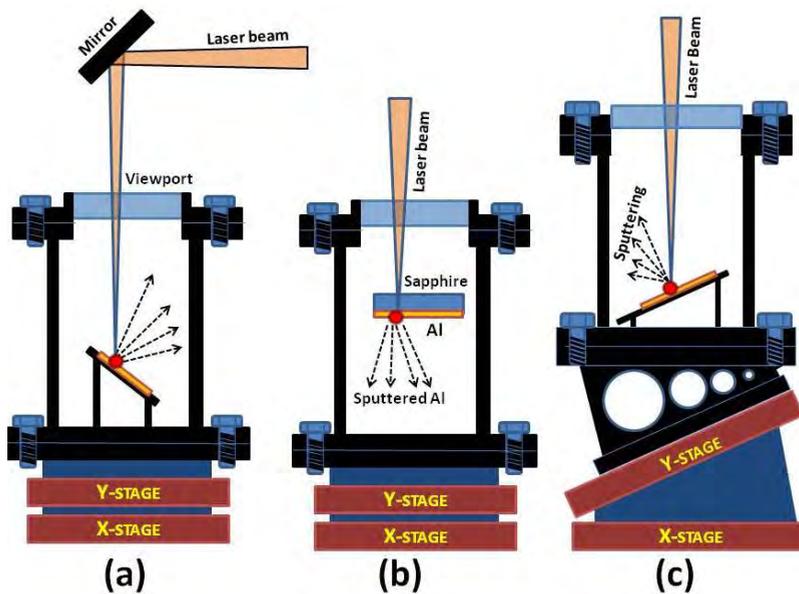


Fig. 3. Three laser extraction cells used for laser extraction of SW noble gases from Genesis Al-collectors. The X-stage moves perpendicular to the figure plane, the Y-stage moves from left to right. The angle between the laser beam and the normal to the ablated surface is  $\pi/4$  in (a),  $\pi$  in (b, but the ablated Al does not reach the viewport) and  $\pi/8$  (c). The cells (a) and (c) were used for ablation of both AloS and PAC, cell (b) is only suitable for AloS and other Genesis SW collectors with transparent sapphire substrates.

heating, reducing the background. All of these improvements have one thing in common: since the sputtered material emerges as  $\sin^2$  of the incidence angle it is highly weighted in a direction perpendicular to the collector surface. By allowing the laser to pass through the viewport and hit the surface at an oblique angle, the sputtered aluminum largely ends up on other parts of the extraction cell, harmlessly away from the vacuum viewport, as shown in the drawing (Figure 3).

### 3.2 Purification of noble gases prior to isotope analysis

Although all of the Genesis collectors are made of ultrapure materials, some terrestrial heavy noble gases may be trapped at the interface between the sapphire substrate and the collector films. This can largely be avoided by refined extraction techniques which avoid that interface. Reduction of terrestrial contamination from material acquired during the hard landing was done by careful cleaning of the PAC to remove as much of this material as possible (Allton et al., 2006; Calaway et al., 2007). However, considering the fragility of the Al films, the AloS collectors were not extensively cleaned. The only surface treatment of the AloS was the mechanical removal of suspicious dust particles and water spots by repeated rinsing with acetone. Contamination was not a problem for the analyses of the abundant light noble gases, but for the less abundant Kr and Xe variable contamination resulted in backgrounds well above the blank levels observed in the same material not flown on the mission. One explanation for the elevated and non-reproducible behavior of the heavy noble gas background was a "brown stain", a thin Si-based polymerized coating, often observed on the flown collectors and other surfaces of the spacecraft (perhaps formed by UV-polymerization of surface contaminants). Ozone plasma treatments reduced Xe and Kr blank to some extent, but the "flown" and "not-flown" AloS collectors still had very different Kr and Xe backgrounds. It was first thought that some of the elevated blanks may have originated from the interface between the Al-film and sapphire substrate, mentioned previously but then why were the flight and non-flight materials so different?

It was finally realized that neither contamination by the "Utah mud" nor the "brown stain", could be responsible for the differences between the noble gas backgrounds of flight and the non-flight AloS collectors but it was the SW-hydrogen, the dominant SW component, that makes the major difference. The huge amounts of SW hydrogen, released during the Al-ablation of the AloS collector, interact with internal surfaces of the vacuum system and the getter material. Surface oxide removal and reduction of reacted getter alloy liberates significant quantities of noble gases which would otherwise be dormant trapped there. Interestingly, ultrahigh vacuum systems are known to be efficiently cleaned with hydrogen at elevated temperatures. Therefore, any SW hydrogen implanted and now released from the AloS must be selectively removed from the vacuum system as quickly as possible to prevent excessive noble gas contamination by such surface "cleaning". To remove the hydrogen, we used a Pd finger, a 5 mm diameter Pd tube with 0.3 mm walls, with the interior exposed to the extraction system and the exterior exposed to the atmosphere, and this solved the problem. When the Pd tube was heated to 500°C it removed 99% of hydrogen from the system to the atmosphere in less than 1 minute. It is interesting that oxygen at atmospheric pressure is needed on the exterior of the tube to remove the hydrogen. The Pd finger was the main modification of the noble gas purification line which otherwise is similar to that used in conventional noble gas mass spectrometry.

### 3.3 Measurements of light noble gases

Precise isotopic analyses of light noble gases require a mass spectrometer with high resolving power (to separate  $^{20}\text{Ne}^+$  from  $^{40}\text{Ar}^{++}$  &  $\text{HF}^+$  and to separate  $^3\text{He}^+$  from  $\text{HD}^+$  &  $\text{H}^{3+}$ ) and a large dynamic range with minimal pressure effects. No commercially available mass spectrometer satisfied our requirements. Therefore, in this study we used a modified  $90^\circ$  magnetic sector mass-spectrometer, the “SuperGnome” (Hohenberg, 1980). It has highly sensitive GS-61 ion source (Baur, 1980), without electron focusing magnet, which results in an extremely small mass discrimination. Because the extraction fields are small and the ions originate on a cone leading to the same trajectory, all of ions have the same energy and follow nearly the same path. This leads to a tight cluster of trajectories, with no removal by source defining slits, so the instrument has a nearly 100% ion transmission. Since few ions are removed by the slits, it also has low memory effects and long useful counting times. In contrast, a widely used Nier-type ion source has significant and often non-reproducible isotope mass discrimination, lower sensitivity and typically 10-50% ion transmission, which implies that 2 to 9 of every 10 ions are wasted.

The disadvantage of GS-61 ion source is caused by the same things as its advantage. Since the ions originate in a region of low electric field gradient, they are slow at being extracted and then follow the same trajectory. Thus, when the pressure is higher the ion density is fairly large, causing space-charge effects. This effect is non-linear with sensitivity, transmission propensity for double charging caused by variable space charge effects in the ionization region. Space charge effects are not present for the heavy noble gases where ion density is low. However, for SW He and Ne, exacerbated by copious quantities of SW hydrogen, space charge effects can be severe and the extended time in the ionization region leads to significant and variable formation of  $^{20}\text{NeH}^+$  which interferes with the low abundance  $^{21}\text{Ne}^+$ . The only way to correct for pressure effects in Ne and He measurements is to match the composition of sample to that of an independently known reference standard. In the course of this study we used artificial mixture of helium isotopes with  $^3\text{He}/^4\text{He} = 6.5 \times 10^{-4}$  (manufactured and certified by ChemGas, France), which is much closer to actual SW ratio than to atmospheric. This helium standard was mixed with atmospheric Ne-He to match SW He/Ne ratio, and with hydrogen to simulate the H abundance in these collectors.

Mass resolution was set to  $\sim 200$  so isobaric interferences from doubly ionized  $\text{CO}_2^{++}$  and  $^{40}\text{Ar}^{++}$  were present on  $^{22}\text{Ne}^+$  and  $^{20}\text{Ne}^+$ , respectively, the latter interference was significantly reduced by running the ion source at 48 eV electron energy. The doubly-charged correction factors were typically  $^{40}\text{Ar}^{++}/\text{Ar}^+ = 0.006$  and  $\text{CO}_2^{++}/\text{CO}_2^+ = 0.02$ . The correction for interferences at  $^3\text{He}$  was more complex since it came from both  $\text{HD}^+$  and  $\text{H}^{3+}$  which are not present at constant proportion and, in fact, also pressure dependent. Luckily, after hydrogen removal, helium becomes the most abundant SW noble gas so the corrections for interference at  $m/e=3$  never exceeded  $\sim 10\%$  and the hydride corrections greatly reduced.  $^3\text{He}/^4\text{He}$  and  $^{21}\text{Ne}/^{20}\text{Ne}$  ratios were corrected for small effects due to high counting rates and deadtime, typically from 10 to 12 ns, corresponding to  $\sim 1\%$  correction at a 1 MHz count rate.

Argon analyses did not present any of these problems because Ar was cryogenically separated from He and Ne (and H) eliminating any of the pressure effects mentioned above. The SW  $^{36}\text{Ar}/^{38}\text{Ar}$  ratio is close to the atmospheric value, and the terrestrial contamination can be accurately subtracted using  $^{40}\text{Ar}$  which is absent in SW in measurable amounts.

Isobaric interferences from HCl on  $m/e = 36$  and  $38$  were very small and, since all of our ultrahigh vacuum pumping lines used oil free scroll pumps, magnetically levitated (lubricant-free) turbomolecular pumps and ion pumps, eliminating most hydrocarbon interferences, the ubiquitous hydrocarbon interference at  $m/e=38$  was not present. All of these factors contributed to the fact that our first measured SW  $^{36}\text{Ar}/^{38}\text{Ar}$  ratio was  $5.501 \pm 0.005$  ( $1\sigma$ ) (Meshik et al., 2007) which remains the most accurate value for SW argon measured to date.

### 3.4 Measurements of heavy noble gases

To measure the isotopic compositions of the heavy noble gases, which are present in such low abundances in the solar wind, a special multi-collector version of the Noblesse mass spectrometer was specially constructed for us by NU Instruments. It utilized a “bright”, Nier-type, ion source with  $\sim 70\%$  ion transmission and unique fast electrostatic zoom lens allowing us to change the effective spacing between isotopes. Since different noble gases have different spacing between the isotopes on the focal plane, variable isotope spacing allows us to use a multiple-dynode collector system to simultaneously measure isotopes of different noble gases. Eight continuous dynode electron multipliers from Burle™, and one Faraday cup collector on the high mass side provided for the simultaneous counting of 9 different ion beams. The high sensitivity of this instrument,  $1.8 \times 10^{-16}$   $\text{cm}^3$  STP  $^{132}\text{Xe}/\text{cps}$  is  $\sim 3$ -times higher than that of the SuperGnome, and the 8 multipliers, made this instrument ideal for the low count rate measurements of Genesis SW Kr and Xe. Moreover, the zoom lens allowed Kr and Xe to be measured simultaneously. However, the miniature Burle electron multipliers are mounted just few mm apart, allowing no room for electrostatic shielding so they do suffer from some crosstalk with  $> 50,000$  count/s ion beams. This configuration is, therefore, not as suitable for He and Ne when a high dynamic range is more important but, for the heavy noble gases, when the counting statistic represents the major source of errors, Multi-Noblesse excels.

The Noblesse mass spectrometer has a counting half-life for Xe of  $\sim 17$  minutes, almost 3 times shorter than SuperGnome instrument, reflecting its higher sensitivity, and its Nier-type source makes memory effects more pronounced in the Noblesse. To minimize these effects, and to correct for them, only small spikes of atmospheric Xe and Kr were ever admitted into this mass spectrometer for calibration and all vacuum lines, extraction, purification and pumping systems were assembled from new parts which were never exposed to any isotopically anomalous noble gases. Whenever possible, these parts were internally electropolished to minimize isobaric contaminations and pumping lines were made as short as possible with no pipes being thinner than  $3/4$ " in diameter for maximum conductance. Additionally, the high voltage power supply for the ion source was modified to be switched on simultaneously with the beginning of measurement, providing a more precise “time zero” when the gas inside the mass spectrometer has not been yet altered by counting and memory growth. The configuration of ion collector for heavy noble gas measurements is shown in Table 1.

There is a potential problem associated with hydrocarbon interference at  $m/e = 78$  due to the omnipresent  $\text{C}_6\text{H}_6$  (benzene) which is not completely resolved from  $^{78}\text{Kr}$ . Attempts to correct for benzene using hydrocarbons measured at  $m/e=79$  and  $77$ , which were measured anyway, (step 4 in Table 1), were not successful. Luckily  $^{78}\text{Kr}$ , the lightest stable Kr isotope,

Magnet, Zoom Lens	Ion collectors (EM – electron multipliers, FC – Faraday Cup):								
	FC	EM1	EM2	EM3	EM4	EM5	EM6	EM7	EM8
B1, Z1		$^{136}\text{Xe}$	$^{134}\text{Xe}$	$^{132}\text{Xe}$	$^{130}\text{Xe}$	$^{128}\text{Xe}$	$^{126}\text{Xe}$	$^{124}\text{Xe}$	
B2, Z2				$^{131}\text{Xe}$	$^{129}\text{Xe}$				
B3, Z3		$^{86}\text{Kr}$		$^{84}\text{Kr}$	$^{83}\text{Kr}$	$^{82}\text{Kr}$		$^{80}\text{Kr}$	
B4, Z4			$^{84}\text{Kr}$	$^{83}\text{Kr}$	$^{82}\text{Kr}$		$^{80}\text{Kr}$		$^{78}\text{Kr}$
B5, Z5	$^{40}\text{Ar}$				$^{38}\text{Ar}$		$^{37}\text{Cl}$		$^{36}\text{Ar}$

Table 1. Assignment of Noblesse ion collectors for Measurements of Genesis heavy noble gases: All isotopes of Xe, Kr and Ar can be measured in five steps of the magnetic field (B) and associated zoom lens (Z) settings. At least one more step (not shown) is needed for the baseline measurement. All Kr isotopes (except  $^{86}\text{Kr}$  and  $^{78}\text{Kr}$ ) are measured twice by different electron multipliers, providing an internal check for the multiplier performance. Switching from one step to another takes less than 2 seconds.

passes through the outermost edge of the zoom lens and, when the electrostatic fringe field of the zoom lens is intentionally distorted, we can measure  $^{78}\text{Kr}$  slightly off-center, where the contribution of benzene is more negligible (Figure 4). This distortion does not affect the other Kr isotopes which pass through the middle part of the lens, but it does provide means for partially resolving the benzene interference and obtaining a valid  $^{78}\text{Kr}$  measurement.

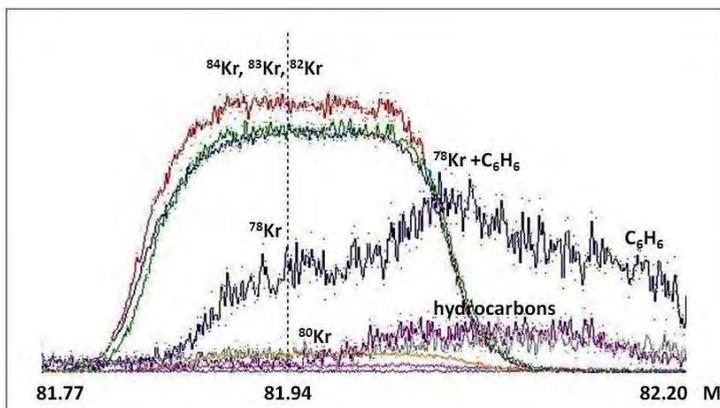


Fig. 4. Simultaneous detection of Kr isotopes 84, 83, 82, 80 and 78. Intentional fringe field distortion of the electrostatic zoom lens allows measurement of  $^{78}\text{Kr}$  without significant benzene contribution. Vertical scales (count rates) are different for different isotopes. Horizontal axis is mass for central (axial) isotope,  $^{82}\text{Kr}$  in this case. The assignment of ion collectors corresponds to step 4 of Table 1.

However, even after solution of the benzene interference problem at  $^{78}\text{Kr}$ , measuring all heavy noble gas isotopes in one run without separation remained difficult because of the limited dynamic range of the miniature electron multipliers and because of the pressure effects in the ion source (although these were much less for the Nier-type ion source in Noblesse than for the GS-61 ion source in the SuperGnome). Additionally, there is the

“change-of-charge” effect that interferes with the measurement of  $^{80}\text{Kr}$ . As mentioned in 3.3, doubly charged  $^{40}\text{Ar}^{++}$  interferes with singly charged  $^{20}\text{Ne}^+$  but another effect of doubly charged  $^{40}\text{Ar}^{++}$  interferes with  $^{80}\text{Kr}$ . A small fraction of  $^{40}\text{Ar}^{++}$  ions can pick up an electron from the source defining slits, becoming  $^{40}\text{Ar}^+$  but with the double energy, thus following the same trajectory as  $^{80}\text{Kr}^+$ . This effect is clearly detectable whenever Kr is measured in the presence of  $^{40}\text{Ar}$ . Therefore, Ar must be cryogenically separated from Kr, although complete Ar removal cannot be achieved without losing a small fraction of Kr and fractionating the rest. At a temperature of  $-125^\circ\text{C}$  for activated charcoal trap  $\sim 2\%$  of the original Ar is still present so an additional measure is required to further reduce the “change-of-charge” effect on  $^{80}\text{Kr}$ . This was done by a reduction of the electron energy from 100 eV to 75 eV at the cost of  $\sim 10\%$  sensitivity loss. Luckily, the solar wind contains very little, if any,  $^{40}\text{Ar}$  so most of the “change-of-charge” problems occur during the calibration of the mass spectrometer.

## 4. Results and discussion

### 4.1 Depth profiles of light noble gases

Measuring the composition of noble gases as a function of implantation depth required a uniform laser ablation of the same area of SW collector with each step incrementally increased in the power density delivered to the target. Our frequency quadrupled NdYAG laser (Powerlite-6030 from Continuum<sup>TM</sup>) delivered  $\sim 10$  mJ of 266 nm in 7ns pulses at 30Hz. The best power stability (shot-to-shot) of 12% (barely sufficient for depth profiling) was achieved only at maximum power and only after about a  $\frac{1}{2}$ -hour “warm-up” period. Several methods were used to control the power: From a pair of rotatable polarizers to attenuating the output power by series of parallel fused quartz plates, each reflecting a few percent of incident beam. However, best results were achieved by selecting delay times of from 125 ms to 300 ms between the flash lamp and the Pockels cell varying the oscillator cavity gain curve of the NdYAG rod.

During the UV-laser step profiling, the laser remained stationary while the extraction cell, mounted on a X-Y-stage moved back and forth (Fig. 3). The stage was programmed to keep velocity constant (typically, 3 mm/s). A fast shutter (computer controlled) blocks the laser during the U-turn of the stage to prevent the power density delivered at the edges of rastered area from increasing beyond that delivered elsewhere. All of the computer codes to control the shutter and the Newport stage via GPIB interface were written in Labview 7.1.

To avoid any contribution of noble gases from the walls of the ablation pit due to stage instability or from beam bleed, with the potential for heating of the un-degassed aluminum adjacent to the rastered area as power increases, each subsequent raster area was made progressively smaller. Therefore, the gas amounts were normalized to the area specific for each step. An example of a completed stepped-power UV laser extraction is shown at the top of the Figure 2d. Depth profiles for He, Ne (preliminarily reported by Meshik et al., 2006; Mabry et al., 2007) and Ar (this work) are assembled in Figure 5.

Solar wind ions are bound to the solar magnetic field and, thus, all ions are implanted with equal velocity so that all SW noble gases (Figure 5) show the same general pattern: The lighter isotopes of each gas ( $^3\text{He}$ ,  $^{20}\text{Ne}$ ,  $^{21}\text{Ne}$  and  $^{36}\text{Ar}$ ) are implanted at shallower depths than the heavier isotopes ( $^4\text{He}$ ,  $^{22}\text{Ne}$ , and  $^{38}\text{Ar}$ ), in general agreement with SRIM-2008 simulations for ions implanted at the same velocity, therefore at slightly different energies.

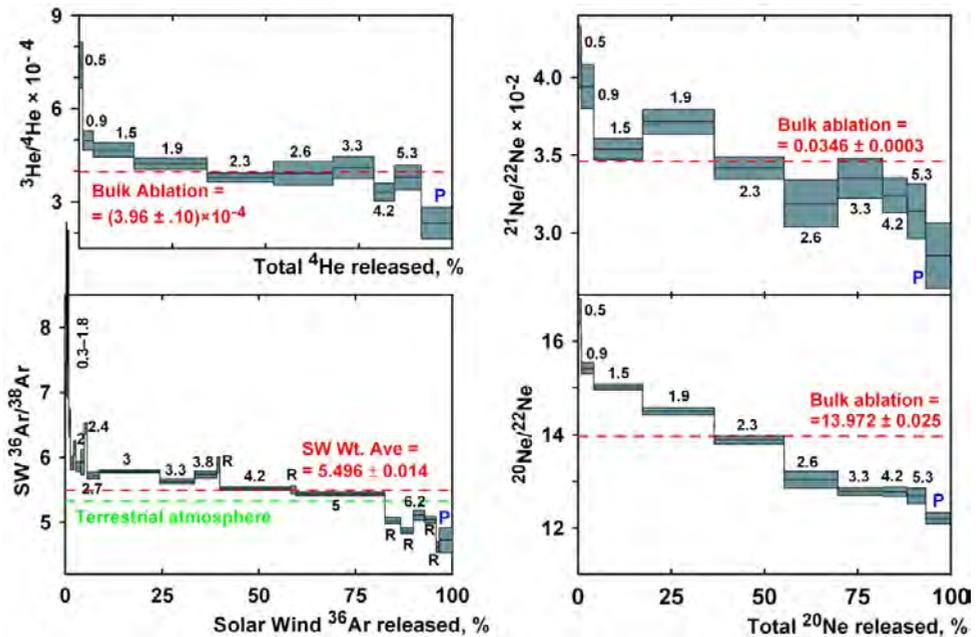


Fig. 5. Isotopic composition of light noble gases extracted from PAC using stepped power UV-laser ablation. Argon in each step has been corrected for the atmospheric contamination assuming that  $^{40}\text{Ar}$  is absent in the SW. He and Ne are not corrected, since there is no way to determine the atmospheric contribution to each individual step. Numbers indicate laser output in mJ, R is re-raster with the same power, P stands for pyrolysis made after the completion of laser ablation. Dashed lines show sum of all steps in Ar plot and bulk IR-ablation values of AloS. Error bars are  $1\sigma$ .

Similar patterns were reported for  $^{20}\text{Ne}/^{22}\text{Ne}$  ratios measured by the CSSE extractions from the BMG (Bulk Metallic Glass,  $\text{Zr}_{58.5}\text{Nb}_{2.8}\text{Cu}_{15.6}\text{Ni}_{12.8}\text{Al}_{10.3}$ ) Genesis SW collector (Grimberg et al., 2006). Analogous isotopic effect has been observed in SW He, Ne and Ar in the lunar regolith samples (e.g. Benkert et al., 1993) and, as we discussed in the Introduction, was interpreted at that time as indicating the presence of two distinct solar wind components: (1) Conventional solar wind, SW, and (2) A more energetic, thus more deeply implanted, high energy tail of the solar wind, referred to as Solar Energetic Particles, SEP. Until recently this interpretation was widely accepted, and even became incorporated into noble gas text books (Ozima & Podosek., 2002; Noble Gases in Geochemistry and Cosmochemistry, 2002) as a distinct component. Very few papers (e.g. Becker, 1995) recognized that solar wind isotope ratios will naturally get heavier with implantation depth. Genesis results clearly support this realization and a distinct SEP component is no longer necessary.

Argon was extracted from PAC using 23 steps of UV-laser ablation with some on them being repeat extractions made at the same output laser power. These were the first analyses made using Noblesse multi-collector mass spectrometer. A record low value for the  $^{40}\text{Ar}/^{36}\text{Ar}$  ratio of 1.12 was found in step #16. This is the most pure SW-Ar (lowest  $^{40}\text{Ar}/^{36}\text{Ar}$  ratio) ever observed for a natural sample, demonstrating the ability of the laser stepped-

power technique to separate SW-Ar from terrestrial contamination, mainly present at the surface of the SW-collector. The total SW  $^{36}\text{Ar}/^{38}\text{Ar} = 5.496 \pm 0.011$  (calculated as weighted sum of all steps) is indistinguishable from  $^{36}\text{Ar}/^{38}\text{Ar} = 5.501 \pm 0.005$  measured in AloS using one step IR-laser extraction (Meshik et al., 2007). Considering that these two measurements were made two years apart using two different mass spectrometers and two different laser extraction techniques, this agreement gives us strong confidence that this is a true SW-Ar composition. Both of these SW  $^{36}\text{Ar}/^{38}\text{Ar}$  analyses agree well with SW-Ar measured independently in different Genesis collectors: AuoS (Gold on Sapphire), DOS (Diamond-like-carbon on Sapphire) and CZ-Si (Czocharalski-grown Si). The timeline of SW Ar measurements (Figure 6) demonstrates the high precision of the Genesis results compared to all of the pre-Genesis measurements. Only after Genesis we can confidently conclude that the SW  $^{36}\text{Ar}/^{38}\text{Ar}$  ratio is significantly higher than that in the terrestrial atmosphere, suggesting atmospheric losses in the early evolution of the Earth's atmosphere.

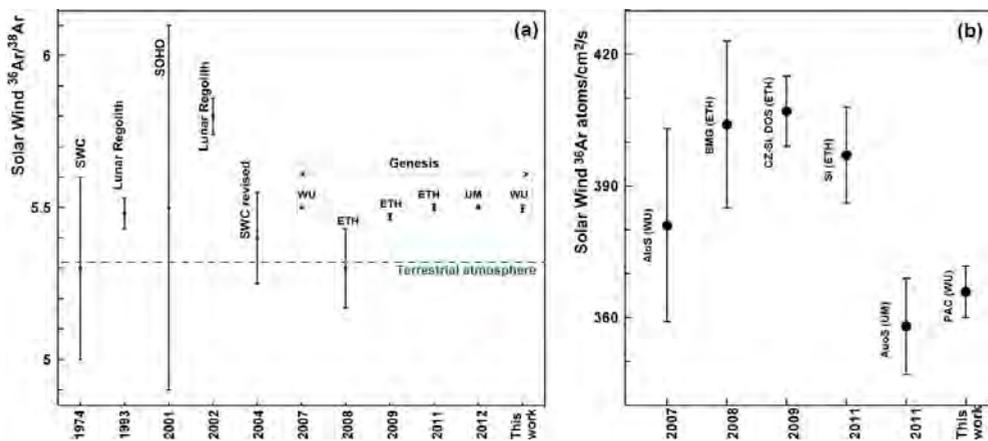


Fig. 6. Comparison of pre-Genesis analyses of SW  $^{36}\text{Ar}/^{38}\text{Ar}$  ratios: (a) (Cerutti, 1974; Benkert et al., 1993; Weygand et al., 2001; Palma et al., 2002; Geiss et al., 2004) with Genesis measurements (Meshik et al., 2007; Grimberg et al., 2008; Heber et al., 2009; Vogel et al., 2001; Pepin et al., 2012; this work). Abbreviations next to Genesis data points stand for laboratories where the analyses were performed: WU - Washington University, ETH - Eidgenössischen Technischen Hochschule Zürich, UM - University of Minnesota. All Genesis results, except for the early, ETH analysis, agree with each other and demonstrate significantly higher precision than those based upon pre-Genesis data. SW  $^{36}\text{Ar}$  fluxes at L1 station (b) are measured in different Genesis targets by different laboratories. All error bars are 1 $\sigma$ .

Solar wind  $^{36}\text{Ar}$  fluxes are in reasonable, although not perfect, agreement (all are within 3 $\sigma$ ). Interestingly, the lower values of SW  $^{36}\text{Ar}$  fluxes are found in metal films (Al and Au) while the 8% higher fluxes are observed in nonmetallic materials (Figure 6). Future experiments will show if this difference is real or an experimental artifact.

The stepped-power laser extraction techniques were developed and refined during the evolution of these Genesis analyses and some of the properties of these techniques were realized only after the experiment was completed. One interesting observation was made

from the pyrolysis of the PAC which had already been degassed by stepped-power laser extractions. Total melting was initially carried out to ensure that all of the SW noble gases had been completely removed by the laser extraction but, as it turned out, this was not the case. Several percent of the SW gases remained present in the PAC even after laser extraction to a depth much greater than the solar wind implantation. UV-laser has sufficient power to extract almost 100% of noble gases from PAC in one extraction step, but when the power increased step-by-step the extraction is no longer complete. About 3.4% of  $^{36}\text{Ar}$ , 6.8% of  $^{20}\text{Ne}$  and 8.3% of  $^4\text{He}$  are still present in PAC after 23-steps of laser extraction (step P in Figure 5) and released only by total pyrolysis of the remaining piece. Interestingly, this is more than it could be expected from SRIM simulations (Figure 1) of the solar wind implantation: so this is an extraction effect, not only an implantation effect. Microscopic observations of laser rastered areas of PAC show that the laser raster did not really make an excavation with a flat bottom, but melted, and re-melted the Al several times, evaporating only a part of it. This heating causes enhanced diffusion of gases in the melt and, since light gases move faster than the heavy ones, more He goes into the remaining Al than Ne (and Ar). In other words, heating from the stepped-power laser technique modifies the original distribution of SW noble gases, making the profile wider and deeper with each step so, in this sense, the technique has some properties similar to traditional step-wise pyrolysis. Therefore, the interpretation of stepped-power laser extractions is not as straightforward as we would like it to be because of the modification of the distribution by the extraction itself and perhaps some fractionation effects since the implanted light noble gases are more easily mobilized. One way to reduce the problem is to use laser pulses much shorter than the 7 ns used in this work to more explosively degas the material without as much heating.

The degree of diffusion losses of noble gases in Genesis SW collectors depends on the material and the thermal history. A step-wise pyrolysis is indicative of such losses. Figure 7 shows the cumulative release of  $^{20}\text{Ne}$  implanted at 20 keV into the different Genesis materials: PAC, AloS and BMG. The first two materials, Al alloy and pure Al, are significantly less retentive compared to amorphous (below~1000°C) BMG. These Ne release profiles can be used to estimate SW-Ne losses in real Genesis materials.

$^{20}\text{Ne}/^{22}\text{Ne}$  ratios and fluxes of SW  $^{20}\text{Ne}$ , measured in the St. Louis, Minnesota and Zürich laboratories, are shown on Figure 8. Although all measured Ne isotope ratios agree to within  $3\sigma$ , there is a trend suggesting that the higher  $^{20}\text{Ne}/^{22}\text{Ne}$  ratios seem to correspond to the higher  $^{20}\text{Ne}$  fluxes, and the PAC seems to suggest a lower  $^{20}\text{Ne}$  flux than either the AloS, BMG or CZ-Si. Given the different thermal diffusion properties of the Genesis collectors (Figure. 7), this seems to make sense. Since exposure times were identical, the lower apparent SW-Ne fluxes indicate some loss of SW Ne. If such losses do occur, the lighter isotope,  $^{20}\text{Ne}$  in this case, will escape preferentially for two reasons: (1) it is implanted at shallower depth and, (2) since it is lighter, it is slightly more mobile than  $^{22}\text{Ne}$ , thus more susceptible to diffusive loss. Moreover, broadening of the original depth distribution will be more significant for  $^{20}\text{Ne}$  than for  $^{22}\text{Ne}$ . This has been confirmed by comparison of two fragments of PAC Genesis sample analyzed at different conditions. One was unbaked prior to analysis, another was kept in vacuum for 10 days at 220°C resulting in a lower  $^{20}\text{Ne}$  content and a lower  $^{20}\text{Ne}/^{22}\text{Ne}$  ratio. A long-term He diffusion experiment in which a sample of PAC was baked at 240°C for 322 days (38% of the duration of the Genesis collector exposure time) showed large losses of He, confirming significant diffusive losses of light

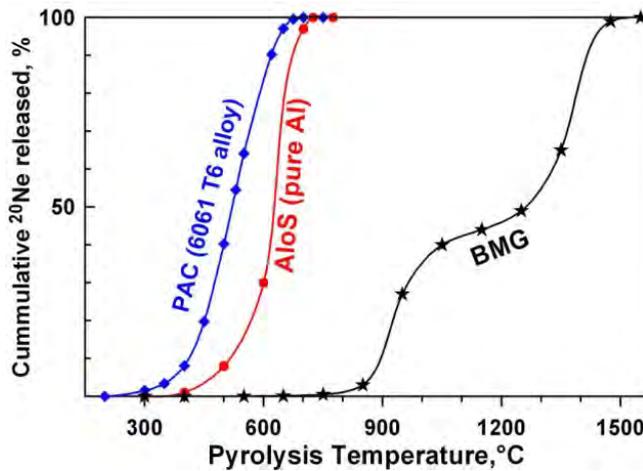


Fig. 7. Release profiles of Ne implanted into different SW collectors at 1 keV/nucleon. Each temperature step was maintained for 30 min. The difference in release curves is the basis for estimation of thermal gas losses and the average temperatures experienced by the Genesis collectors.

noble gases from the PAC although, in that experiment, Ne was not measured (Mabry, 2009). These observations, and the verifying experiments, all point out that some Ne losses, and consequent isotope fractionation, must have occurred with the PAC collector. Although the “low”  $^{20}\text{Ne}/^{22}\text{Ne}$  ratios observed in the PAC agree more closely with the previous “lunar” ratios (cf. Benkert et al., 1993), we believe the higher  $^{20}\text{Ne}/^{22}\text{Ne}$  ratios observed in the AloS collectors, being less modified; provide a better measurement of the modern solar wind. Given a solar wind flux of about  $10^7$  protons/cm<sup>2</sup>/s, lunar surface material is quickly saturated with solar wind hydrogen to the point that, without extensive diffusive redistribution, the implanted solar wind hydrogen atoms will outnumber the host lattice atoms in a broad region near the end of its range in only a few tens of years. This means, among other things, extensive lattice damage and enhanced surface erosion with associated effects on the diffusion and retention of the implanted light noble gases. We, therefore, expect large and variable diffusive losses from lunar soils and regolith samples. In addition, even though the foils were carefully cleaned, the Apollo Solar Wind Composition Experiment is still susceptible to contamination by fine lunar dust that contains both diffusively modified solar wind Ne and spallation-produced Ne. Thus, we conclude that AloS, CZ-Si and DOS measurements should provide the definitive composition of the modern solar wind Ne. However, the Ne measured in the Zurich laboratory in the Si and DOS collectors, which are expected to be equally retentive, appear to be slightly heavier than those measured in the AloS collectors (St. Louis) and in the AuoS collectors (Minneapolis), as shown in Figure 8. At present time we do not have a reasonable explanation. However, a higher resolution ( $\sim 1500$ ) mass-spectrometer is expected to be installed at Washington University in the future, it will be capable of resolving  $^{40}\text{Ar}^{++}$  from  $^{20}\text{Ne}^+$ , removing one of the uncertainties in Ne analysis. Re-analysis of Genesis SW neon using this instrument will provide an opportunity for better precision and exploration of any apparent discrepancy in the SW  $^{20}\text{Ne}/^{22}\text{Ne}$  ratios obtained by the different laboratories.

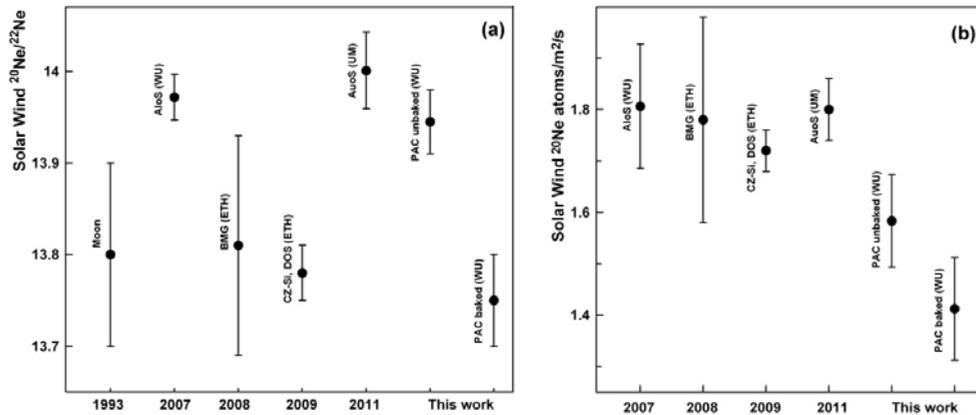


Fig. 8. Solar wind  $^{20}\text{Ne}/^{22}\text{Ne}$  ratios (a) and  $^{20}\text{Ne}$  fluxes at L1 station (b) measured by different laboratories in different Genesis SW-collector materials. All abbreviations are the same as in Fig. 6. “Lunar” SW-Ne is from Benkert et al., 1993. A diffusion experiment demonstrates that PAC kept in vacuum for 10 days at 220°C may lose some Ne, preferentially  $^{20}\text{Ne}$ .

Helium is the most abundant noble gas in the SW. It is also the lightest, the most susceptible to diffusive loss and, because it has the largest relative difference in masses of its two isotopes, it is the most indicative of isotopic mass fractionation. All Genesis He analyses and some “pre”- Genesis results are shown in Figure 9. Both isotope ratios and apparent SW He fluxes are scattered much more than would be justified by the statistical uncertainties.

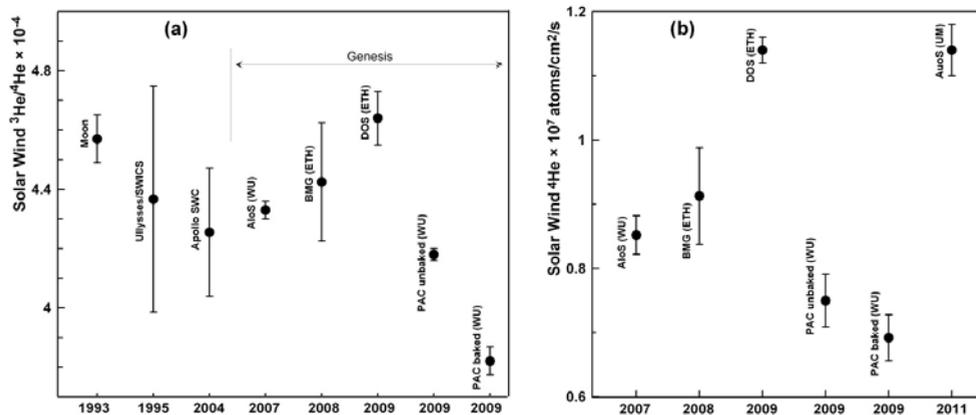


Fig. 9. Isotopic compositions (a) and fluxes (b) at the L1 point measured in different Genesis SW collectors in St. Louis, Minnesota and Zürich labs. Lunar and Apollo SWC SW data are from Benkert et al., 1993 and Geiss et al., 2004. The 500 day average He composition from Ulysses/SWICS is from Bodmer et al., 1995. Aluminum collectors (both AloS and PAC) are from Mabry et al., 2007 and Mabry., 2009. PAC (baked) was kept at 240°C for 322 days, ~38% of total Genesis collection time. Helium losses from all Al-collectors are evident and apparently are accompanied by preferential losses of  $^3\text{He}$ .

Systematical errors, not reflected in the data, evidently exist in this figure. Both types of Al collectors have significantly lower concentrations of SW-He (Figure 9b), demonstrating the diffusive losses expected from the thermal release profiles shown in Figure 7. The AloS and the PAC have the lowest  $^3\text{He}/^4\text{He}$  ratios observed among the SW collectors and pre-Genesis SW-He determinations, suggesting that aluminum diffusively loses He at the temperature of the exposed collector surfaces and, as expected from the diffusive properties shown in Figure 7, the PAC loses more He than the AloS collector.

The real-time diffusion experiment conducted by Mabry (2009) confirms the poor SW-He retention properties of the PAC at the elevated collection temperature. Both the  $^3\text{He}/^4\text{He}$  ratios and the He concentrations (reflecting apparent He fluxes) were significantly lower following a 322 day vacuum bake (38% of the Genesis mission) at 240°C. Even the unbaked reference sample of the PAC demonstrates the lowest measured apparent He fluxes and  $^3\text{He}/^4\text{He}$  ratios indicating significant He losses during the Genesis collection period, not surprising since the temperatures of Genesis PAC and AloS collectors were estimated to be around 165°C (Mabry, 2009). Therefore, none of the Genesis aluminum collectors completely retain solar wind He or preserve the original  $^3\text{He}/^4\text{He}$  ratios, both can only be considered as lower limits. Among the other SW-He collectors, DOS (Diamond-like Carbon on Sapphire) CZ-Si (Czochralski-grown silicon) and gold (both AuoS and foil), DOS is probably the best choice since it does not require as high backscattering corrections (up to 35% for Au). AloS however do not demonstrate significant Ne losses and completely retain SW Ar. Therefore, AloS was the choice material for analyses of SW heavy noble gases.

## 4.2 Heavy noble gases

The large concentration of the light SW noble gases He and Ne in the Genesis collectors meant that corrections for atmospheric or other contaminations were usually negligible. Argon from the collectors contained significant terrestrial contributions but since the solar wind has negligible  $^{40}\text{Ar}$ , and the terrestrial isotopic ratios are well known, this can easily be removed to leave pure solar wind argon. For krypton and xenon, which are far less abundant in the solar wind, the terrestrial contamination becomes a serious problem and there is no “terrestrial only” isotope to identify the trapped component. In fact, the compositions of SW and terrestrial noble gases are not significantly different so partitioning by isotopic composition is not possible. Our original intention was to use stepped-power laser extraction to separate any superficial surface-correlated contamination from the more deeply implanted SW noble gases. A complicating factor is the low abundances of the heavy noble gases in the SW which requires analyzing very large areas of the collectors for precise measurements in stepped-power laser extractions. The conventional way to document terrestrial Xe and Kr contributions is to analyze reference (non-flight) SW collectors, manufactured in the same way as the flight collectors, utilizing the same procedures and raster areas. The Xe and Kr signals measured in these non-flight coupons would then be a proxy for blanks in the actual collectors. Unfortunately, the AloS collectors were manufactured in several batches and after the “hard” landing of the Genesis return capsule it became challenging to pair flight and non-flight AloS material. That said, a more severe problem was found. In the laser extraction experiments it was observed that the Xe and Kr blanks were neither proportional to the raster areas nor were they very reproducible. It was soon realized that the large quantities of implanted SW hydrogen released from SW

collectors reacted with the getter material. Since the SAES getters were produced by sintering in an inert atmosphere, this liberated dormant Xe and Kr from the getters. The quantity of hydrogen was so large that it could not be separated cryogenically in the sample system. Removing hydrogen from the flight tube using palladium (described in 3.2) significantly reduced this problem, but did not eliminate it completely, so new techniques for minimizing terrestrial noble gases had to be developed.

The alternative approach for blank correction is based on the significant difference in  $^{84}\text{Kr}/^{132}\text{Xe}$  ratios between the terrestrial atmosphere (27.78; Ozima & Podosek., 2002) and the solar wind (9.55, Meshik et al., 2009). In the case of binary mixtures of SW and terrestrial components, the  $^{84}\text{Kr}/^{132}\text{Xe}$  can be used as a measure of terrestrial contribution. Since the Washington University multi-collector mass spectrometer, the laser extraction cells and the purification system have never seen any isotopically anomalous gases, we are limited to these two compositions (with negligible mass fractionation). A capability to simultaneously measure both heavy noble gases in a single run (3.4) was needed to use this approach, but this was the plan all along. Laser extraction was done in a single step using maximal power to ensure the complete extraction of SW noble gases, to provide maximum signal and to minimize the analysis time. Xe and Kr were cryogenically separated from at least 98% of the Ar using activated "Berkeley" charcoal finger kept at  $-125^\circ\text{C}$ , which reduced the change-of-charge effect at  $^{80}\text{Kr}$ . Both PAC and AloS collectors were analyzed in different laser cells (shown in Figure 3) using pulsed laser extraction at two wavelengths: 266 nm for PAC and 1064 nm for AloS. It was realized that Kr and Xe may not be trapped in atmospheric proportion, with Xe usually more "sticky" than Kr, but it was assumed that they would probably not be isotopically fractionated to any significant degree (an assumption that could be checked later). To determine the actual trapped  $^{84}\text{Kr}/^{132}\text{Xe}$  ratio we assumed that, for all 24 samples analyzed, this ratio was constant. Equations (1) and (2) describe binary mixtures between SW and terrestrial trapped gases for each measurement:

$$^{84}\text{Kr}_{SW} = ^{84}\text{Kr}_M \times \left[ \left( \frac{^{132}\text{Xe}}{^{84}\text{Kr}} \right)_M - \left( \frac{^{132}\text{Xe}}{^{84}\text{Kr}} \right)_T \right] / \left[ \left( \frac{^{132}\text{Xe}}{^{84}\text{Kr}} \right)_T - \left( \frac{^{132}\text{Xe}}{^{84}\text{Kr}} \right)_{SW} \right] \quad (1)$$

$$^{132}\text{Xe}_{SW} = ^{132}\text{Xe}_M \times \left[ \left( \frac{^{84}\text{Kr}}{^{132}\text{Xe}} \right)_M - \left( \frac{^{84}\text{Kr}}{^{132}\text{Xe}} \right)_T \right] / \left[ \left( \frac{^{84}\text{Kr}}{^{132}\text{Xe}} \right)_T - \left( \frac{^{84}\text{Kr}}{^{132}\text{Xe}} \right)_{SW} \right] \quad (2)$$

Here SW refers to Solar Wind, M to Measured and T to Trapped (or Terrestrial) and the two unknowns are  $(^{132}\text{Xe}/^{84}\text{Kr})_{SW}$  and  $(^{132}\text{Xe}/^{84}\text{Kr})_T$ . With two equations only two measurements are needed to determine the values for these ratios but, for the 24 measurements available, the system is over-determined. A multi-variance solution is obtained from minimization of the standard deviations of the SW fluencies and the most probable values for  $(^{132}\text{Xe}/^{84}\text{Kr})_{SW}$ , and correspondingly,  $^{132}\text{Xe}_{SW}$  and  $^{84}\text{Kr}_{SW}$  were obtained. The best convergence, shown in Figure 10a, was achieved at  $(^{84}\text{Kr}/^{132}\text{Xe})_{\text{trapped}} = 24.4$  (Figure 10b), only 12% lower than the terrestrial atmosphere, a value confirming our assumption of no significant isotopic mass fractionation in this component.

All Kr and Xe isotopic analyses are shown in Figures 11 and 12, respectively, and Table 2 presents final results. All of the data in these figures show consistent results even though

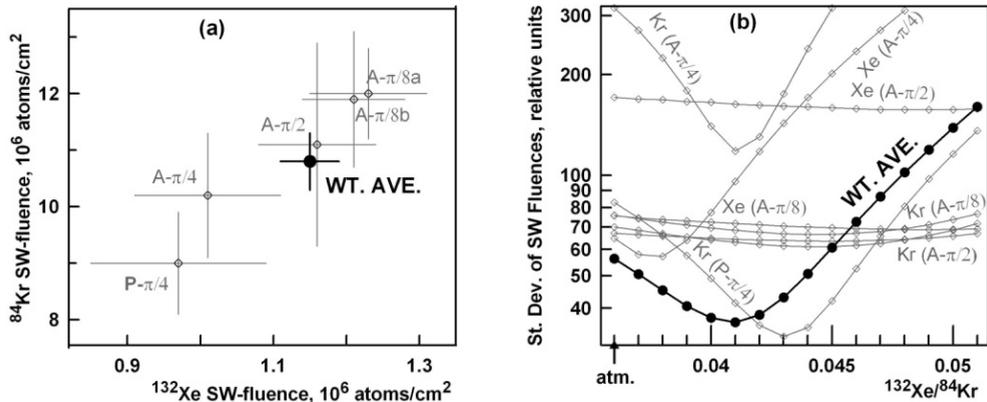


Fig. 10. The best convergence of SW fluencies (a) has been achieved at  $^{132}\text{Xe}/^{84}\text{Kr} = 0.041$  (b), providing our current fluence estimate:  $(1.15 \pm 0.04) \times 10^6$   $^{132}\text{Xe}$  atoms/cm $^2$  and  $(1.08 \pm 0.05) \times 10^7$   $^{84}\text{Kr}$  atoms/cm $^2$ .

$^{86}\text{Kr}$	$^{84}\text{Kr}$	$^{83}\text{Kr}$	$^{82}\text{Kr}$	$^{80}\text{Kr}$	$^{78}\text{Kr}$
.3012 (4)	$\equiv 1$	.2034 (2)	.2054 (2)	.0412 (2)	.00642 (5)

$^{136}\text{Xe}$	$^{134}\text{Xe}$	$^{132}\text{Xe}$	$^{131}\text{Xe}$	$^{130}\text{Xe}$	$^{129}\text{Xe}$	$^{128}\text{Xe}$	$^{126}\text{Xe}$	$^{124}\text{Xe}$
.3003 (6)	.3692 (7)	$\equiv 1$	.8263 (13)	.1649 (4)	1.0401(10)	.0842 (3)	.00417(9)	.00492 (7)

Table 2. Isotopic composition of heavy noble gases in solar wind measured in aluminum Genesis collectors. Errors are  $1\sigma$ .

they represent both types of aluminum SW collectors, were analyzed in different extraction cells under different conditions, using two different pulsed laser wavelengths, and were performed several months apart.

The isotopic composition of solar wind heavy noble gases from the Genesis collectors (this work) can be compared with solar wind Xe and Kr previously inferred from lunar surface material (c.f. Pepin et al., 1995, Figure 13).

A few first-order observations can be made: The isotopic ratios of heavy SW noble gases implanted by lunar regolith over millions of years are indistinguishable from the contemporary SW observed in the Genesis collectors to within  $< 1\%$ . This sets an upper limit to possible temporal variations of SW Kr and Xe. The small isotope differences we do observe suggest that SW-Kr inferred from the lunar regolith is slightly heavier than that we measure in Genesis while no such trend is observed for Xe. SW compositions inferred from lunar regolith may be more subjective to systematic error, and they are less precise than those measured by Genesis, at least at the major isotopes. For instance, the trend we see in this comparison is suggestive of some diffusive loss of Kr from the lunar regolith, not the case for the more retentive Xe. However, in order to test whether this effect is real, Kr compositions inferred from the lunar regolith should be revisited.

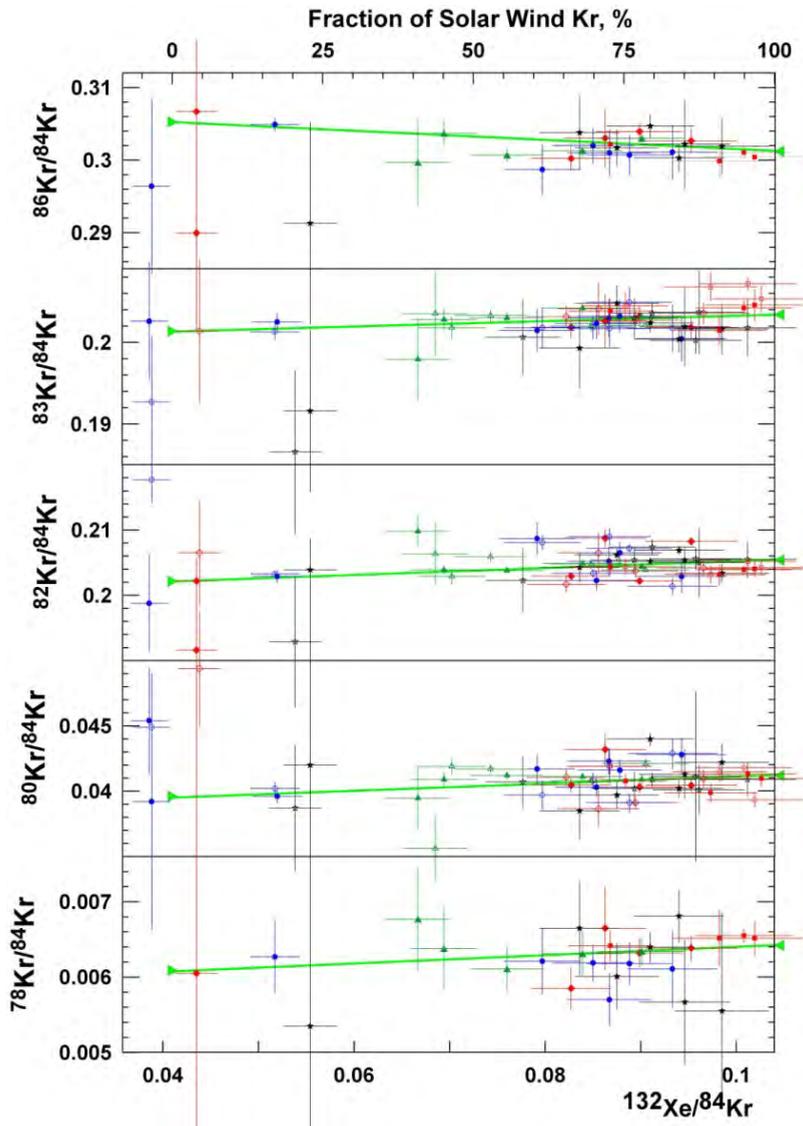


Fig. 11. Kr isotopic composition measured in Genesis Al collectors. Fitting line forced through the estimated trapped component, the ordinate intercept gives isotopic composition of the solar wind. Different colors correspond to different experimental conditions, which within statistical errors result in the same SW composition.

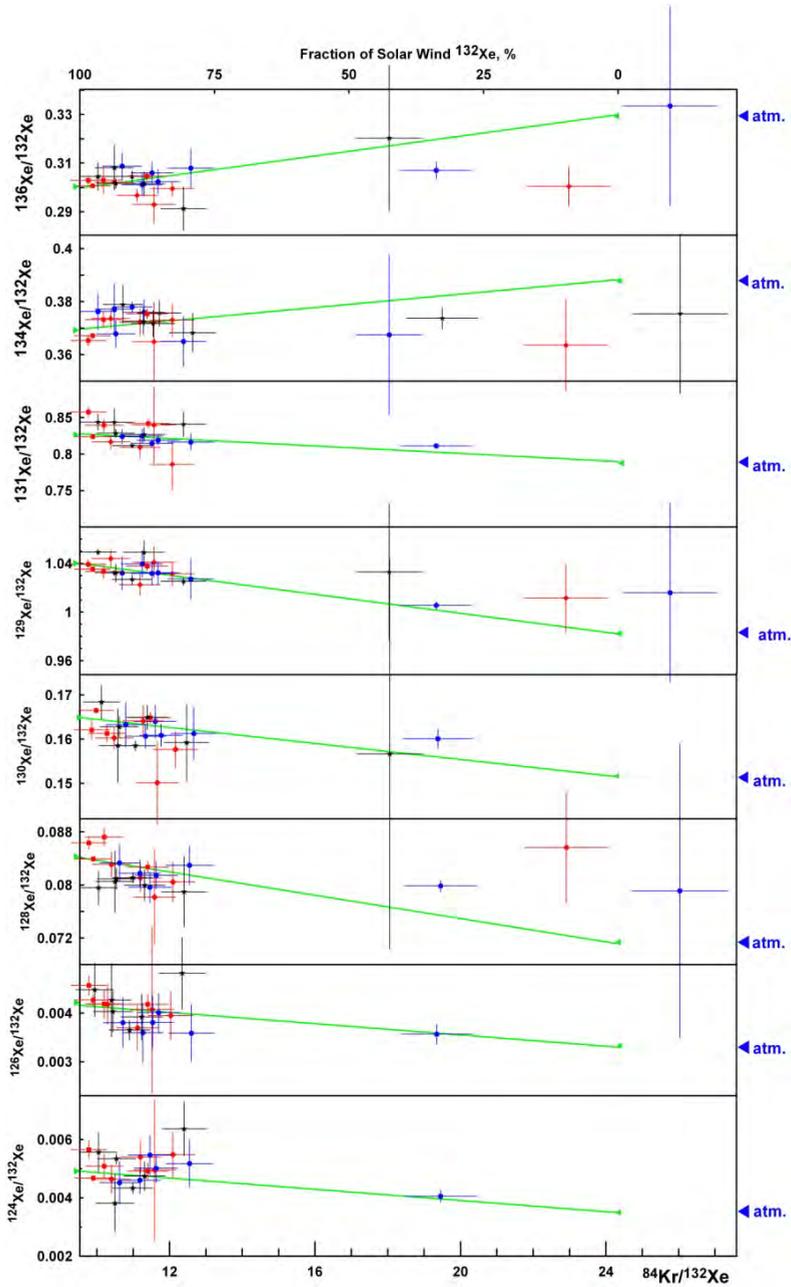


Fig. 12. Xe isotopic composition in Genesis Aluminum collectors. Fitting line forced through the estimated trapped component, ordinate intercept gives isotopic composition of the solar wind. Different colors correspond to different experimental conditions.

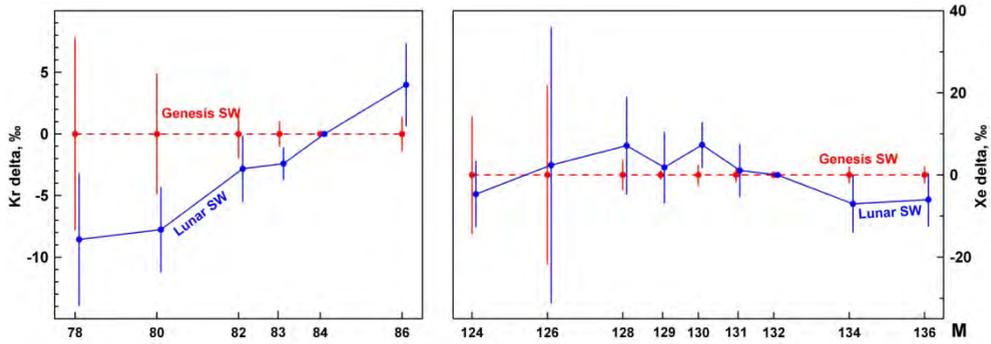


Fig. 13. “Lunar” SW (Pepin et al, 1995) vs. Genesis SW (this work). Although normalized to the Genesis composition as a delta plot, the errors shown ( $1\sigma$ ) are not propagated, so overlapping errors infer consistency.

## 5. Conclusion

Depth profile of solar wind argon retrieved from Genesis A1 collector confirms the isotopic fractionation which occurs during implantation at constant velocity, an effect previously observed for helium and neon. This eliminates the need for a unique heavy SEP noble gas component thought to be required from analyses of lunar surface material. New, more precise Ar analyses, and recent results from two independent laboratories, confirm our earlier published value for the  $^{36}\text{Ar}/^{38}\text{Ar}$  ratio in the solar wind. The unique analytical capability developed at Washington University to simultaneously analyze all Xe and Kr isotopes allows us to determine the composition of heavy noble gases in the solar wind to a precision exceeding previous values inferred from lunar surface material.

## 6. Acknowledgments

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