



Semiannual Science Report to NASA May 2010 D. S Burnett and Genesis Science Team

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What: Mission in a Nutshell

 Placed a spacecraft outside the terrestrial magnetosphere

Exposed Materials

- Solar wind ions (keV/amu) implant and stick
- Exposed for 27 months
- Fluences low, so materials must be ultrapure.
- Returned materials to Earth for analysis in terrestrial laboratories.



Why: Genesis Science Objectives

- Provide solar isotopic abundances to level of precision required for planetary science purposes.
- Provide greatly improved knowledge of solar elemental abundances.
- Provide a reservoir of solar matter to meet the needs of 21st century planetary science.
- Provide elemental and isotopic data for the 3 different types ("regimes") of solar wind.



Solar Wind Regimes

- Three different kinds ("regimes") of solar wind:
 - High speed (coronal hole)
 - Low speed ("interstream")
 - Coronal Mass Ejections
- Genesis separately sampled each of 3 solar wind regimes as well as bulk solar wind:
 - Allows correction for differences in composition between sun and solar wind
 - Agreement in derived solar composition from different regimes validates correction procedures



Interstream (Slow)

Coronal Mass Ejection (Closed field lines)



The Genesis Payload

Canister and Collector Materials pre launch



Concentrator: Focusing Ion Telescope





Concentrator Cross-section

H⁺ Rejection Grid 0.1-3.5kV





Purpose of the Concentrator (LANL)

- Increase the Concentration of Solar Wind Ions Relative to the Background Contamination
 - Specifically for Oxygen and Nitrogen
 - Also for Any Other Elements < about 36 AMU</p>
 - Mass range verified by post-recovery analysis
 - Four target 30mm radius quadrants.
 - C Excluded Due To Its Presence In Target Materials:
 - Silicon Carbide (O)
 - 13C CVD Diamond (O)
 - Amorphous Diamond-like-C Film on Si (N)
 - Small areas of bare Si: C isotope analyses may be possible.
 - Average Concentration of 20x Over Whole Target
 - Designed to Reject 93% of Protons to Avoid Radiation Damage
 - Limitations in flight rejection grid voltage lowered this to about 85%
- Mass fractionation can be well characterized to attain precise isotope ratios (see O isotope section).



Analysis Overview

- Genesis sample analysis is proceeding on a broad front in 26 laboratories worldwide.
- Rates vary, but progress is being made; 2009-2010 is a particularly good period.
- The goal of Genesis is quantitative data; great emphasis on getting numbers right.
- A major advantage of sample return missions is that important data can be verified, and in most cases, replicated with different techniques.
- A major effort has been to make accurate, replicated measurements of the fluences of Mg and Ne. Most techniques can analyze one of these elements, which will then constitute primary quantitative reference fluences for other elements.



Analysis Overview, con't

Two distinct requirements:

- Extract implanted solar wind from collector materials.
- Analyzed extracted solar wind.

Can mix and match approaches for extraction and analysis. Mass spectrometry is the most widely-used analysis technique.



Science Team Analysis Methods

- Secondary Ion Mass Spectrometry (SIMS)
 - Solar wind extracted by ion beam sputtering
- Gas Source Mass Spectrometry
 - Extraction by laser ablation or chemical etching (HNO₃, Hg)
- Resonance Ionization Mass Spectrometry (RIMS)
 - Extraction by ion beam sputtering
- Total Reflection X-ray Fluorescence
 - in-situ analysis; unique in not requiring extraction.
 - essentially non-destructive.
- Inductively-coupled Plasma Mass Spectrometry
 - Extraction by differential chemical etching or laser ablation.
- Accelerator Mass Spectrometry
 - Extraction by differential chemical etching.
- Radiochemical Neutron Activation Analysis
 - Extraction by differential chemical etching.



Solar Wind O Isotopic Composition

- This is our highest priority science objective.
- Three of the four quadrants in the concentrator target were designed to support O isotopic analyses.
 - SiC (2)
 - 13C CVD diamond (1)
 - All of these quadrants were unbroken in crash.



As recovered, concentrator target holder; broken quadrant is diamond-like-carbon



O isotopes: Genesis Advanced Analytical Instrument Facility: UCLA MegaSIMS





<u>GENESIS</u> MegaSIMS O Isotopic Analyses McKeegan, Kallio, Heber; UCLA

Genesis analytical instruments are Ferraris'. They are marvelous when they work, but they spend a lot of time in the garage.

After a long period of repair, upgrading, and testing, the MegaSIMS is on the road again, running at top performance.

New analyses (2010 LPSC) on the SiC Concentrator target 60001 subsequent to those reported in McKeegan et al (2009 LPSC) confirm the results reported therein.



Solar Wind O profile in target SiC. UCLA MegaSIMS. (McKeegan, et al. LPSC 09, 10 or App. Surf Sci 255, 1461, 2008)



The MegaSIMS is a Genesisdedicated instrument. The front end is a standard SIMS instrument in which O- ions are produced by sputtering of the SiC sample with 20 keV Cs+ primary ions. However, instead of just measuring the low E ions, they are accelerated to MeV energies. The acceleration destroys all interfering molecular ions, in particular the 16OH interference with 170. After acceleration, the ions are mass-analyzed and counted with standard accelerator mass spectrometry techniques.



Low E Cs sputter cleaning of 180 implant into SiC.

60001 was ultrasonically cleaned in xylene. Residual surface contamination was removed by sputter cleaning with low energy (5 keV) Cs. This produces an acceptable loss of about 20-25 nm, but results in the clean SW 16O profile shown in the figure in the previous slide. Instrumental background, as measured at depths beyond 300 nm, was reduced to an almost-negligible level by a cryo-pumped vacuum below 1e-11 torr.



In (a), 16O surface contamination is important at depths as large as 50nm; however, this represents ion beam mixing of a thin layer of surface contamination to larger depths by the 20keV Cs primary ion beam. Sputtering with 5 keV Cs ions (b) removes the
surface contamination but this is accompanied by much less mixing Fig (b) is the depth profile measured with 20keV Cs after the preclean with a depth scale corrected for loss during precleaning. The contamination background at depths greater than 25nm is greatly reduced.

•60001 SiC Concentrator target All profiles



Group averages (all profiles from a given target radial distance)

Variation in del180 with distance is due to concentrator instrumental mass fractionation. Concentrator fractionation is mass dependent, so capdel170 is precisely measured.



Distance from concentrator center (mm)

Measure concentrator mass fractionation with 20Ne in 60001; same sample as O Zurich ETH: Heber et al., 2010 LPSC.

Noble gas analysis spots



Detail, Area A

Noble gases released by UV (213nm) laser ablation

Ne: 70 x 70 μ m² rastered pits, equally distributed over radius, ultra-sensitive mass spectrometer

➔ narrow sampling, multiple analyses for statistics

He, Ne, Ar: 400 x 400 μ m² rastered pits, 4 positions, normal mass spectrometer





Ne fluences: measured in SiC



(DOS, Heber et al. 2009 in press GCA 2010)



le isotopic composition in SiC as function of the target radius



This isotope fractionation curve is applied to O to correct for instrumental mass fractionation imposed by concentrator

Mean values from 3 – 4 analyses Error = 1σ stdev Sigmoidal fit, 95% confidence band

Bulk solar wind ²⁰Ne/²²Ne: Genesis, Heber et al. 2009



Is Ne fractionation directly applicable to correct for N, O fractionation? Assess with theoretical profiles.

Modeled $\delta~$ (‰/ amu)



Modeling by R Wiens (LANL) Modeled ≠ measured Ne fractionation pattern (previous slide) But can use for relative comparison Accordingly, isotope fractionation is similar for N, Ne and O

> Therefore, apply Ne fractionation factor directly to O



60001 corrected for concentrator mass dependent fractionation



O Isotope Summary

We have a clear solar wind signal, background corrections are acceptable. The experiment worked.

- The Earth and bulk meteorites (inner solar system) are depleted in ¹⁶O by ~60 to 70‰ relative to the Sun and the bulk composition of the solar nebula
- Correction for mass-dependent fractionation in the concentrator gives the bulk solar wind O isotopic composition (previous slide).
- Possible isotopic fractionation between the Sun and the solar wind must be addressed (following slides)



Isotopic Fractionation (Wiens et al., LPSC 2010)

- Data:
 - Mid 1990s: When GENESIS was proposed, there was no clear evidence for isotopic fractionation
 - 1998-2005: Slight evidence from in-situ spacecraft for fractionation, but error bars were huge
 - 2007: Significant differences in solar-wind regimes for HeNeAr from GENESIS samples (see Heber et al LPSC 2008, abs 1779)
- Theory:
 - FIP suggests no isotopic fractionation
 - Large fractionations suggested by Coulomb drag model (next slide).



Coulomb Drag (Bochsler 2000 model)





60001 corrected for solar wind - Sun fractionation



O Isotope summary

• Sun-Solar Wind isotope fractionation moves measured Genesis solar wind point towards the CAI trend line.

• Correction based on Bochsler Coulomb Drag (BCD) model puts Sun (solar nebula) to high del 180 sign of the CAI line.

• Reason to believe that BCD model overcorrects. So, plausible that solar nebula lies on CAI line.

- Key test: Mg isotopes. BCD model predicts 8 permil/amu fractionation.
- Except for some CAIs, mass dependent Mg isotopic variations in inner solar system material are less than 1 permil/amu.

• So Terrestrial Mg isotopic composition should be equal to Sun, so solar wind – Earth Mg isotope fractionations equals Sun-solar wind differences.

- An 8 permil/amu fractionation should be measurable even with SIMS.
- Analyses are in progress.



Solar N Isotopic Composition

This is our #2 science objective.



The isotopic composition of N shows wide variations in solar system materials. Focus here on Earth-Jupiter difference.



Work prior to 2010

Nancy (Marty et al., GCA 74, 340, 2010)

- Laser ablation of Au from the concentrator target holder ("Au cross")
 - Recovery as molecular N₂
- Target holder not intended for this analysis, so background contamination N_2 is high.
- Ratio of SW to contamination N evaluated by comparing measured Ne/N ratio to solar wind fluence ratio.
- Maximum amount of SW N only about 3%, but
- significant decrease in del15N seen consistent with SW N having same, very negative, del15N as Jupiter (about -400 per mil).

Minnesota (Pepin et al; LPSC 2009 abstract)

- Au on sapphire (AuoS) array collectors exposed to Hg vapor at room T
- N released as N₂ upon amalgamation. Good recovery yields from implants.
- Blanks very low
- But, many flight samples release essentially no N !
- The few flight samples that release N show del15N of about +150-200
- Strong disagreement with Nancy result.



MegaSIMS N analysis (Kallio, McKeegan, Heber (LPSC 2010)

Extract secondary CN- mass 26 & 27 for acceleration (28,29,30Si- blocked off)



Simultaneous counting in multicollector

<u>GENESIS</u>

Solar Wind N profiles in 60001 Concentrator SiC

MegaSIMS conditions:

5 keV Cs⁺ pre-cleaning of the surface 300x300 μm^2

20 keV Cs⁺ depth profiling with optically gated raster 150 x 150 μm^2

multicollection by two electron multipliers with shielding from "crosstalk"

std-sample bracketing using N-doped SiC disc








Conclusions

Solar wind nitrogen signal to background ratio is very good using MegaSIMS and SiC sample 60001

There is still a large uncertainty ($\pm \sim 100$ ‰) due to instrumental effects. Also only five depth profiles have been measured (versus 40 for oxygen(. This will be significantly reduced in future analyses.

Genesis SiC concentrator sample 60001 gives solar wind ¹⁵N/¹⁴N within uncertainty of ¹⁵N/¹⁴N in Jupiter's atmosphere and TiN from a CAI

Nitrogen on Earth is heavy in same sense as Ne: evidence for significant early loss of terrestrial atmosphere?



#3 Measurement Objective: Noble Gas Elemental and Isotopic Analyses

Summary of work published or submitted.

Ne in Genesis Bulk Metallic Glass. SEP component doesn't exist. Solves long-standing lunar problem (ETH Zurich).

Grimberg et al. Science 314, 1133, 2006.

Proc. Symp. Comp. of Matter symposium, 3 papers.

Space Sci. Rev. vol 170, 2007.

Reisenfeld et al Solar Wind Conditions for Genesis samples, based on monitor data along with other spacecraft data for the same period.

Wiens et al Genesis Solar Wind Overview

Heber et al. Genesis Concentrator Performance Based on Ne Analysis of the Target Holder Gold Cross.

Ne and Ar isotopic composition of different regimes (Wash U), Meshik et al., *Science* 318, 443, 2007

This paper produced additional favorable technical summaries: Science 318, 401, 2007 Nature News 17 Oct 2007 nature.com/news/2007/071018/full/news.2007.175.html\



Published work on noble gases, con't

Solar wind noble gases in targets from the Genesis mission PhD thesis, Ansgar Grimberg, ETH Zurich, 2007.

- Wieler et al., Consequences of the non-existence of the SEP component for noble gas geo- and cosmochemistry. *Chemical Geology* 244, 382, 2007.
- Grimberg et al. Solar wind He, Ne, and Ar isotopic and elemental composition. Data from the metallic glass flown on the NASA Genesis spacecraft. *Geochimica, Cosmochemica Acta* 72, 626, 2008.
- Heber et al. Noble gas composition of the solar wind as collected by the Genesis mission. In press, Geochimica, Cosmochimica, in press 2010.



From: Heber et al (2010). Noble Gas Isotopic and Elemental Composition in Bulk Solar Wind.



Samples (diamond-like-carbon shown here) are laser ablated to release HeNeArKrXe for mass spectrometric analysis.

Image shows pits from HeNeAr analyses. Those for KrXe are 3-7 times larger, given low fluences.

All noble gas laboratories analyzing Genesis samples extract using laser ablation. Mass spec techniques vary.



Meshik et al. Wash U Simultaneous multi-collection of Kr isotopes:



LPSC2010



Heavy noble gas analyses of polished Al collector (PAC; slide 8)

Bulk material and procedural blacks (no laser) are very low (<<5% of SW)

Surface blank is significant and not easily separable by stepped UV-laser extraction.

Non-flight material blank is smaller that the blank in flown SW-collectors. Future samples that are uvozone cleaned to remove brown stain may give lower blanks.

Released SW-H apparently cleans oxidation layer from internal surfaces of the vacuum system liberating otherwise dormant noble gases. Pd-filter and new vacuum pump mitigates this problem.

This work:SW collector = PAC 4 different areas (0.4 – 1.8 cm²)Number of extraction steps = 2 (surface and bulk)

Red points: Genesis PAC Kr isotope data.



PAC data are consistent with a mixture of atmospheric surface contamination and the lunar regolith solar wind from Pepin et al (1995) but not with the solar Kr isotopic composition derived from a gasrich meteorite by Pedroni and Begemann (1994). The same conclusion is drawn from correlation plots based on other Kr isotopes. The PAC data agree with the Genesis ⁸⁶Kr/⁸⁴Kr from Heber et al (2010)





The best estimates of Genesis solar wind Kr isotopic composition comes from correlation lines relative to ¹³²Xe/⁸⁴Kr which is very different in the solar wind and the atmosphere and for which a Genesis measured value is available.



Isotopic fractionation of solar wind and atmospheric Kr



the generally minor effects of uncertainties in relative spallation yields (Table 4D).

Superposition of Genesis PAC data (red points) on literature compilation of measurements of solar Kr isotopic composition expressed as % deviation from terrestrial atmospheric Kr.

The PAC data for ⁸⁰Kr are high, being affected by charge exchange ⁴⁰Ar contributions.

Although not as precise as some literature analyses with larger amounts of Kr, Genesis data are interpretationally clean as samples of solar wind Kr.

for etch fractions 3-4 and 3-10 from 79035 ilmenite) in the others. Plotted errors for this latter group do not include fractionated solar Kr.



Wash U conclusions:

- We identified and corrected all major experimental problems, optimizing our multicollector instrument for simultaneous analyses heavy noble gas isotopes in Genesis SW-collectors.
- Behavior of Kr and Xe blanks in Al collector has been investigated and now we fully realize (although not completely understand) the complexity of blank correction.
- Xe/Kr ratio may provide a useful way to correct individual extraction steps for blank to obtain Solar wind Kr isotopic composition.
- Our results suggest that present day SW-Kr is isotopically light (compare to terrestrial) in a good agreement with SW-Kr found in lunar and meteoritic regolith samples. Possible differences at mass 86 may be important.
- This agreement points to time-invariant Kr isotopic structure of SW, as all lunar regolith Kr samples refer to at least 10⁸ yr ago.

The apparent excess of ⁸⁰Kr is not SW but due to "change of charge" ⁴⁰Ar, where mass 40⁺⁺ loses an electron on the source slit and goes through the magnet as 40⁺ with doubled energy. Calibrations will allow corrections to be made.



Xe isotopic composition Crowther and Gilmour, U. Manchester

RELAX = resonance ionization laser ablation mass spectrometric analysis of Xe.

- Exceptional sensitivity: detection limit ~ 950 atoms ¹³²Xe
- Best blank ~ 1000 atoms ¹³²Xe
- Samples restricted to < ~ 10⁶ atoms
- Xe extracted by IR laser step heating.
- Sum results from large number of ≈ 3 mm Si samples
 crash has supplied many of these.
- UV laser ablation depth profiling offers better discrimination of solar wind Xe from Xe impurities in Si collectors and surface contamination Xe.
 - 1st pulse = surface contamination
 - Next 10 pulses mostly solar wind
 - Subsequent set of 10 pulses = background Xe in Si.





71501 ilmenite – Wieler & Baur 1994, Pepin et al. 1995





Relax Summary

- Full-beam ablation
 - ~30 shots extract all gas from flight samples
- Observe variable concentrations of Xe
 - Both flight and non-flight samples
 - Variation in the flight samples in consistent with the variation in the non-flight samples
 - ¹³⁶Xe hint of some other contribution in flight sample?
 - Mixing line approach provides basis for deriving SW Xe isotopic composition.



Science Issue: Do Sun and solar wind have same *elemental* composition?

- Spacecraft data have shown that high first ionization potential (FIP) elements e.g. He are depleted in solar wind compared to solar surface (photosphere).
 - e.g. He/Fe is lower in SW than in photosphere.
- Data for most easily-ionized elements (FIP < 9eV, e.g. Fe) appear unfractionated.
 - Most of elements in terrestrial planets have FIP<9eV</p>
- Genesis will provide a better test, but never will escape need to know a few photospheric elemental ratios accurately.
- If fractionations due only to first ionization potentials, solar wind and photosphere isotope ratios expected to be same.



Fractionation Factor

F = (X/Mg)_{SW} / (X/Mg)_{photosphere}



FIP Plot from spacecraft data





GENESIS Solar Wind physical parameters affecting element fractionation. (Wiens et al., LPSC 2010)

- First ionization potential (FIP)
 - High FIP elements depleted by ~2x relative to low FIP elements in interstream wind. Relatively little fractionation in coronal hole wind
- First Ionization Time (FIT)
 - Time required to ionize an element under a given condition
 - Takes into account electron and UV photon impact rates as well as FIP
- Fractionation plots vs FIP or FIT similar but have significant differences.



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FIT (first ionization time) plot from spacecraft data

FIT is more physical than FIP, but is model-dependent. Ulysses data plots using FIT are cleaner than those with FIP with the 9eV fractionation cutoff (translated to about 10- 20 sec ionization time) showing clear depletions of high FIP/FIT elements, but no evidence of fractionation among low FIP/FIT elements. Errors in SW abundances about 20%; errors in photosphere 10-20%. Note that Mg and Fe have same FIP but different FIT



Heavy Noble Gas Elemental Abundances Vogel et al., LPSC 2010 ETH Zurich

Analyses (all CZ-Si):

14 Bulk targets: ^{36,38}Ar, ^{84,86}Kr, ^{129,132}Xe 3 slow SW targets (L): ³⁶Ar, ⁸⁴Kr, ¹³²Xe 2 fast SW targets (H): ³⁶Ar, ⁸⁴Kr, ¹³²Xe 3 CME targets (E): ³⁶Ar, ⁸⁴Kr, ¹³²Xe



Gas extraction: Measurement:

UV-Laser ablation (λ : 213 nm; 4-50 mm²) Peak jumping

Blank correction: Procedural blanks, material blanks, re-extractions Blank contributions to samples gas amounts: ³⁶Ar ~ negligible ⁸⁴Kr ~ 5% ¹³²Xe ~ 10%



Element ratio Ar/Xe

Spacecraft data indicate that fractionations not same in different solar wind regimes. Better definition of Genesis regime dependences of elemental fractionation will lead to better theories of the mechanism(s) of fractionation and their magnitudes.

He/Ne, Ne/Ar data show fast and slow SW about same (Heber et al., LPSC 2008, abs 1779), but CME systematically enriched in lighter element.



Element ratio Ar/Kr



- Slow > CME OK
- Bulk SW ³⁶Ar/⁸⁴Kr: 2411 (64)
- Fast SW ratio too low
- → Fast SW ³⁶Ar/⁸⁴Kr suffers from high ⁸⁴Kr. Surface contaminaiton?
- → To obtain good mass balance: ³⁶Ar/⁸⁴Kr in fast SW ~2700

Interpretation of solar wind noble gas abundances complicated because, except for He, there are no true photospheric abundances.



Secondary Ion Mass Spectrometry (SIMS) Essentials (e.g. Mg)

- Sample sputtered with O2+ ions, sometimes in presence of O₂ flood gas for Si.
- Analyses at ASU (Jurewicz, Guan, Hervig), UCLA (McKeegan, Heber), CIW (Wang, Nittler), and Caltech (Guan)
 - All SIMS instruments, but different design.
 - replicate analyses by different instruments; unique feature of sample return missions:
 - Mg+ ions produced and analyzed with mass spectrometer.
- Measure Mg relative to matrix ion:
 - Si or C from Amorphous diamond-like-carbon (Sandia).
 - Verify accuracy by replicating results on different materials
 - better quality data is a major feature of sample return missions.
- Data from 30-50 micron-size areas; particulate contamination avoided.
 - Many analyses possible even for small samples.
- Depth profiles acquired in 5-10 minutes, (after hours of tuning).
- Quantitation simple in principle; relative to lab implant standard.



Beautiful depth profiles for Mg in Sandia diamond-like C and Si collector materials (Jurewicz et al, ASU)





- Details of analyses in Nov. 2007 GPMC; not repeated here.
- Major discrepancy in Mg fluence between Si and DOS (Sandia) when "external" implant standard used.
- Discrepancy eliminated by implanting known fluence of ²⁵Mg as internal standard into flight samples.
- Unlike Mg, good agreement for Fe fluence obtained between two materials.
- Total Reflection XRF (APS ANL; Kitts et al) Fe fluence agrees with SIMS result.
 - Kitts et al. Application of grazing incidence XRF techniques to discover and quantify implanted solar wind. *J. Applied Physics* **105**, 64908, 2009.



Compare with CI chondrites



Most compilations of "solar" elemental abundances based on CI chondritic meteorites. Justification for this is agreement with photospheric abundances. Genesis Fe/Mg, at present, distinct from CI ratio, but systematic errors in implant fluences must be assessed before final conclusions drawn. Goal will be to maintain precision as on figure, but Fe/Mg value could change.

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Improved method of implant fluence calibration.

Fe implant fluences independently verified with RBS; problem has been with Mg.

Possible discrepancies up to 40%; see slides 40-47 in 5/09 GPMC.

New approach (McKeegan):

- If implant fluences spatially homogeneous, different materials present in implant see same fluence.
- Implant minor isotope (e.g. ²⁵Mg) into glass of independently known (and microscopically uniform) Mg concentration.
- Known ²⁴Mg concentration gives SIMS sensitivity factor.
- Fluence and bulk Mg selected to clearly measure ²⁵Mg implant profile above uniform background ²⁵Mg (next slide).
- Implant fluence calculated from integrated background-corrected ²⁵Mg profile.







Srni IV NIST 617 Implant Fluence calibration.

Profile on previous slide.

NBS 617 has about 35 ppm Mg. Accurate measurement of amount in progress by isotopic dilution by Ngo and Papanasstasiou.

Nominal 25mg implant fluence = 3e13/cm².

Except for small differences in backscattering, measured glass fluence applies to Si and diamond-like-C implanted along with glasses.

Si sample CZ4A was surrounded by three pieces of NIST 617. Relative fluence of 3 glasses agrees to better than 5%. Fluence of CZ4A will be accurately calibrated.

Using CZ4A, accurate SIMS intercalibration possible for previous implants used in Genesis sample analysis



Resonance Ionization Mass Spectrometry (RIMS) essentials.

- RIMS analysis begins with sputtering with a primary ion beam, like SIMS.
 - However, only roughly 1/1000 of the atoms sputtered are the ions utilized by SIMS.
- RIMS ionizes the sputtered neutral species by timing ionizing laser pulses with an ion beam pulse with mass analysis by time-of-flight mass spectrometry.
 - Laser duty cycle limits acquisition time, presently 1 to 2 kHz
- A very large fraction (>1%) of the neutrals can be ionized and counted, producing very high sensitivity.
 - About 20% has been demonstrated for Mg.
- The photoionization takes place in two steps.
 - One laser frequency is highly tuned to excite the selected atom into an excited state. This
 provides high selectivity of the element being analyzed from any molecular ions of the same
 mass.
 - A second laser ionizes the excited atom which is detected by the time of flight mass spectrometer.
- A RIMS instrument designed specifically for Genesis samples is operating at ANL.
 - See Veryovkin et al., LPSC abstracts
- At present, both SIMS and RIMS are useful for Genesis samples, but eventually only RIMS will be able to analyze elements of low abundance.
 - Present detection limit is below 50 ppt.



ANL RIMS Ca profile



Figure shows processed bulk solar wind ⁴⁰Ca depth profile for sample 60179 . Analyses on 130x260 micron spots.

Profiles are based on normalizing the RIMS Ca counts to non-resonant ²⁸Si photoion counts. Small corrections have been made: (a) for drift between Genesis and implant standard based on a secondary standard and (b) for SIMS ion background. A larger, constant, correction of 3e14/cc has been made which may represent Ca impurities in the Si. Similarity of the two 60179 and

predicted SW depth profies ("Chad") clearly shows that solar wind is being measured.

New 3 element (MgCaCr) analysis scheme has been developed. New 3 element implant standards have been made and will be standardized using glasses of known Ca (as with Mg above) (Jurewicz, ASU). Unfortunately, many samples show much more Ca (and Cr) surface contmination than 60179.



RIMS upgrades

A major instrument upgrade is in progress designed to minimize effects of surface contamination by (1) better analytical depth resolution, (2) minimizing counts from surface contamination from regions outside analyzed spot, (3) SEM imaging of sample to avoid particles, and (4) improved preanalysis sample surface cleaning by CO_2 foam and acid cleaning, verified by TRXRF analyses (see later section).

(1) At a given depth, a pulsed ion beam is used for the RIMS analysis. A DC ion beam is used to sputter to a deeper depth within the sample. Previously a single beam was used for both modes. Now a separate lower energy DC ion beam will be used which will have much less ion beam mixing of surface contamination into the solar wind layers. The pulsed beam will retain higher energy to provide adequate sputtering rate.



(2) Improved RIMS spatial resolution



As shown in the figure, a focused ion beam is used to dig a trench around the area to be analyzed which occupies a "mesa" inside the trench. Surface contamination is removed from the trench, minimizing background from any stray ions reaching outside the area of the mesa.

DC sputtering uniformly reduces the height of the mesa. The pulsed beam is focused to the center of the mesa, as shown.

In future analyses, further spatial resolution will achieved by rastering the pulsed beam, and accepting counts only near the center of the raster (gating).



Bulk solar wind O, C fluences



C and O are relatively easily measured by spacecraft instruments, but difficult for Genesis because of surface contamination and instrumental background problems. SIMS sensitivity is adequate.

The figure (log scale) shows where we started in 2005.

The structure at small depths is due to transient sputtering effects. The deep tail reflects O from small (<100A) particles mixed to larger depths by the Cs primary ion beam with an exponential "gardening" profile.

In this experiment, chemical etching with $HF-H_2O_2$ reduced the surface contamination by about a factor of 3, but the residual signal was still two orders of magnitude higher than the expected solar wind levels.

At depths greater than 1000 A, the residual instrumental background, after sputtering away surface contamination, is still 10x the solar wind.


C and O fluences by backside depth profiling (Heber, Guan, Jurewicz)

- A standard SIMS analytical approach by the semiconductor industry for shallow depth profiling is to analyze toward the surface from the back of a sample thinned to a few microns thickness.
- The thickness uniformity tolerances for the thinned sample, as well as those for sputtering during the SIMS analysis, are very high in order to avoid having one part of the rastered primary ion beam break through to surface contamination while most of the sputtering is within the implanted solar wind.
- Flight bulk SW Si sample 60757, along with a ¹³C implant sample was thinned to a nominal 1.5 microns by Evans Analytical Labs. The samples were epoxied onto a 7 mm square Si substrate prior to thinning.
- SIMS analyses were done on the CalTech 7f.
- Sample 60757 appears to be only about 0.32 to 0.34 microns thick instead of 1.5, but this is still useful
- See Heber et al LPSC 2010 and MetSoc 2010 abstract.



Bulk SW C depth profile.



Depth scale inverted. Measurement begins on back side (large depths).

Backside surface contamination sputtered through by about 2500A (800A from back surface)

Depth scale calculated from time at which breakthrough of surface C observed. This gives some error in depth scale.

Overnight sputtering with Si reduces instrumental background to low levels (2000-2500 A region.

Essentially pure solar wind from 300-400 to 1300 A.

Modeling of initial 300A, lost in onset of breakthough, required. Accuracy of theoretical profile (Chad) important.



Bulk SW O depth profile



O and C measured simultaneously. see discussion on previous slide.

C and O profiles similar. Not obvious in data plotted here, but O breakthrough always precedes C even though cps C/cps O from epoxy is roughly 4. So O breakthrough not due to epoxy.

Possibly early O breakthrough due to oxidized fractures. If fractures occurred during sample thinning, a thicker sample than 60757 might give better results and preparation of a new sample is in progress.



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FIT plot from Genesis data

- We can combine the noble gas and Cr fluences from the Aug 2009 GPMC with the Mg and Fe fluences from the May 2009 GPMC and produce a preliminary FIT plot using only Genesis data.
- Backside depth profiles for C and O are good enough that preliminary estimate of bulk solar wind fluence possible, so these have been added.
- Mg is used as normalizing element. Note that most literature FIP/FIT plots use O as the normalizing element. Errors in either the Genesis Mg fluence or the photospheric Mg abundance only affect the value of F for other elements. The pattern of points on the plot is unaffected.

Ne and Ar are not plotted, as there are no spectroscopic data for their photospheric abundances.

- Kr and Xe are special cases. There are no spectroscopic photospheric abundances; however, Cl abundance curves are sufficiently smooth in the Xe, and especially Kr, mass regions that interpolation gives relatively precise abundances subject to two assumptions:
- 1) the overall validity of CI abundances.
- 2) the assumption that Kr and Xe, as volatile elements, are not depleted or enhanced relative to neighboring nonvolatile elements.

Genesis can eventually test both of these assumptions.

Light element photospheric abundances are too variable to interpolate abundances for Ne and Ar.





Genesis FIT plot: interpretation

The red lines are obviously not a unique description of the data, but represent an interpretation commonly used for spacecraft data.

As more and better Genesis data are obtained, the true systematics of the data will be revealed.

As noted earlier by Vogel et al (LPSC 09), the solar wind Xe/Kr is significantly higher than the interpolated solar ratio. This is an issue deserving of further study.



Cleaning up to Recover Science after Crash

Three necessary steps to recovery of science objectives:

Recover Collector Materials intact. Done
 Expected 250 samples, have ~ 15,000 > 3mm; 1700 > 1 cm .
 Priority given to allocation, but major progress made on catalogs, see Genesis JSC web page.

2. Remove surface contamination. Required for essentially all analyses, especially from here on out.

3. Learn to allocate and analyze smaller samples than planned. Items 2 and 3 worked simultaneously.



Basic Approach:

- Contamination levels are highly variable.
- Cleanliness requirements vary for different analytical techniques.
 No one-size-fits-all solution.
- Basic Curatorial cleaning services: UPW, uv-ozone.
- Rest is responsibility of PIs
 - but Curatorial Facility supports with characterization
 - Particle counting (JSC)
 - Ellipsometry (JSC)
 - XPS (EAG commercial lab)
 - Lab TRXRF (new; see following pages)
- Ellipsometry doesn't work for some materials and doesn't give quantitative information.



Brown Stain (slide unchanged from previous GPMCs)

Non-crash issue

- Polymerized organic contamination film ('brown stain")
 - Thicknesses measured by ellipsometry (JSC,) XPS (EAG, JPL), and FIB/TEM (LLNL).
 - -Up to about 75 A thick, but
 - Highly variable; some samples appear essentially free of stain.
- If less than 100A: negligible SW attenuation (C. Olinger, LANL calculations).
- Brown stain must be removed for most, but not all, analyses:
- uv-ozone (demonstrated by Open U) most successful to date.
 - JSC unit is operational and demonstrated to remove C effectively
 - For some applications, greater amount of removal may be required.
 - good correlation between XPS and ellipsometery on same Si samples.

We have learned to work around Brown Stain.

Important Boundary Condition:

• Because amounts of contamination highly variable, cherry-picking "good" (low brown stain) samples is an acceptable contamination control.



Particulate Contamination Overview.

Crash-related issue: Particulate contamination on all samples.

- Variety of wet cleaning techniques work to varying degrees:
 - Any solvent (e.g. ultra pure water) will take off 1/2-2/3 of particles and almost all big (>5 micron) ones.
 - For most samples, JSC Megasonic ultra-pure-H2O (UPW) in routine use for materials for which this possible.
 - Probably not applicable for AloS samples and must be done with care for AuoS
- Particulate contamination is the major obstacle to completion of the Genesis science objectives.
 - Our success so far has been with techniques such as SIMS or RIMS that can analyze areas of 50-200 micron size, can dodge micron-size particles and can recognize, and afford to lose, a particle-contaminated profile.
 - None of these benefits are available for large area analysis (> 1 cm size), for which in some cases a single contaminant particle can ruin the analysis.
 - Some of the science objectives require analysis of large areas.
- Some success with acid cleaning, but not good enough. Systematic approach needed.



<u>GENESIS</u>

Master Plan for Sample Cleaning





Master Cleaning Plan

Although we know a lot about particulate surface contamination, we don't know enough to successfully clean samples for large area analysis.

- We need approach(s) capable of efficient before-after measurements on samples subject to various wet cleaning techniques.
 - Analysis must be non-destructive; need to be quantitative but high accuracy not required.
 - Efficiency and access important because a lot of trial and error will be required in wet cleaning tests.

We need to do a large number of analyses.

XPS used previously does not have adequate sensitivity for elements other than C or O.

- But XPS remains our best technique to measure brown stain.

Synchrotron radiation TRXRF (SRTRXRF) (APS) and TOFSIMS (Manchester) have adequate sensitivity.

Genesis time for SRTRXRF (K Kitts) only a few days per year. Need to emphasize solar wind analysis.

Access to Manchester TOFSIMS has been good, but not possible to process a large number of samples solely for cleaning studies.



Laboratory TRXRF

- Use tube X-rays rather than synchrotron radiation (SRTRXRF); otherwise technique is same as described in previous GPMC.
- XPS detection limits are ~ 10¹⁴ atoms/cm²
- SRTRXRF has ~ 10¹⁰ atoms/cm² atoms/cm² detection limits.
- Lab TRXRF ~ 10¹¹- 10¹² atoms/cm² detection limits achievable because of good signal/background and use of 10⁴ - 10⁵ sec counting times.
- Minimum sample handling; samples analyzed, as received, in air.
 - Samples handled in laminar flow benches.
- TRXRF demonstrated to work on all collector materials (except diamond-like-C for unknown reasons).
- Not sensitive for elements lighter than Si; works best for 1st row transition elements (Ca-Ge), but samples clean of all these elements is way beyond where we are now.
- Lab TRXRF analyses by M. Schmeling (Loyola U, Chicago)



Master Plan, JSC roles.

- Samples for cleaning studies selected by Curatorial Facility with concurrence of Allocation SubCommittee when large samples (> cm size) involved.
- Flow chart is for "research" stage, i.e. trying to devise wet cleaning procedures to remove contamination at the lab TRXRF level.
- When feasible, some small-sample iterations with PI analysis lab desirable to know when sample is "clean enough" of element(s) to be analyzed.
- "Success" is research stage producing TRXRF-clean samples by the end of 2011.
- After that, we would consider going into a "production" mode, generating a set of clean samples stored at JSC, available for future allocation.
- Ultra-pure water (UPW) cleaning is routine for all collector materials except AloS and AuoS. Removes particles larger than 5 microns along with Utah salts.
- UV-ozone works for all materials, even Sandia diamond-like-C.
 - Pre-launch, only CZ Si documented to have clean surfaces for many elements at 10¹⁰ atom/cm² level.
 - Pre-launch surfaces of some materials, e.g. sapphire, now known to be relatively dirty.
 - Thus, brown stain is deposited on top of pre-launch surface contamination and must be removed. UV-ozone accomplishes this.
 - SiO₂ residue from silicone component in brown stain. Dilute HF will have to be the first step in all wet cleaning procedures. Possible for all but AloS collectors.



Master Plan: Wet Cleaning

At least 3 labs (CalTech, ASU, FSU) are involved in the wet cleaning phase. All three use clean labs and high purity reagents.

- The general procedure will be for JSC-cleaned samples to be sent for Lab TRXRF. Analyzed locations (2-3 mm) recorded so that the same spot can be re-analyzed after wet cleaning. Typically 3 spots per sample.
- Most collector materials are chemically inert, so cleaning trials to date have used acids, with recipes derived from the semiconductor literature.



Master Plan: SEM analyses.

- When a given cleaning cycle has not produced a lab TRXRF-clean sample, we will use SEM examination in many cases to determine the chemical/mineralogical form of the resistant element.
- Many collectors are conducting, allowing particles to be measured directly on the samples.
- Zn and Ga are ubiquitous contaminants from a white paint used for thermal control in the Sample Return Capsule The Zn and Ga in the white paint are in the form of $ZnGa_2O_4$ which is very insoluble. Analyzing Zn and Ga is not a high science objective of Genesis, but there may be other elements in the white paint. If necessary, these can be characterized on available paint coupons, starting with XPS.
- Somewhat surprisingly however, acid cleaning has been successful in removing Zn and Ga from sapphire and Si-on-sapphire (SoS) collectors.
- If acid-insoluble white paint removal becomes important, the acetate peel technique (Kuhlman) is the only approach we know of at present. Acetate peeling may be the only technique available for AloS (Al on sapphire) collectors.
- Sandia diamond-like-carbon cannot be measured by TRXRF. SEM examination of wet cleaned samples necessary. Removal of N-bearing heat shield C particles is important. uvO₃ may do this, but checking required.



Master Plan: lab TRXRF-clean samples

When we have produced a sample that is lab-TRXRF clean, this is when we will spend our capital with the most sensitive SRTRXRF techniques or TOFSIMS. We already have several TRXRF-clean samples.

If the lab TRXRF-clean samples are not clean enough, we will need to seek greater access to TOF-SIMS instruments.

Following 2 slides show TRXRF spectra for the same spot on sapphire sample 60242. Overall we have TRXRF data on 15 samples and controls.

As shown for 60242 we have had good results with simple dilute HCI cleaning.

Analyses are made in air, so there is an air Ar peak in all spectra.

The pre-cleaned spectra show relatively large amounts of S, Ca, Fe, Hf, Zn, Ge, and Pb.

Large Ge peaks are ubiquitous, arising from powdering of almost all of our Ge collectors in the crash. It has turned out to be very easy to remove the Ge as illustrated in the after HCI cleaning spectrum.

The S and Ca are probably Utahogenic. HCl cleaning has been effective in removing these

Si is insoluble in aqua regia. Aqua regia cleaning studies on Si by Humayun have shown that there is a good correlation of Fe and Cr indicating a finely powdered stainless steel component. Stainless steel particles have been seen in SEM studies. HCI cleaning has usually been effective in removing Fe and Cr, but some Fe remains on 60242 after HCI

Other samples show clear TRXRF Zn and Ga peaks indicating white paint; however, there is at least one sample with a large Zn peak and no Ga, so there are other sources of Zn contamination.

A wide variety of "exotic" contaminants are observed, like the Hf in 60242. In addition to Hf, there has been Ir, Os, Sn, and Bi, presumably from the sample return capsule. These have been effectively removed by HCI.

The Pb is of unknown origin and is difficult to remove.

Other samples are both better and worse than 60242.



After HCI Cleaning





Cleaning Summary

As of mid 2010, we are well into the TRXRF study. There has been enough success with dilute HCI cleaning that this is the acid of choice at present.

As all samples analyzed have not been treated in a standard manner, we are uniformly treating all samples: $uvozone(JSC) \rightarrow dilute HF$ (Caltech; removes SiO2 from brown stain silicones) \rightarrow HCI (CalTech) \rightarrow TRXRF.

Cleaning with supercritical CO_2 is being tested.

In parallel with flight samples, flight spare controls are being analyzed. These have been quite clean. This shows that our packaging, shipping, and handling procedures are not adding significant inorganic surface contamination.

Limits of aqua regia cleaning in terms of TRXRF roughening, as suggested by previous SRTRXRF studies, will be determined.

Negligible erosion of solar wind is expected from these procedures, but SIMS checks of SW Mg profiles, where the profile is well known, will be made.

If acid cleaning alone fails, we will explore the use of crown ethers successfully used by Nishiizumi in removing Utah mud from SRC lid foils.



<u>GENESIS</u>

Top Level Status Summary (unchanged)

- The bar has been raised considerably by crash, but not giving up on any of our measurement objectives.
- Particulate contamination remains our biggest challenge, but
- Optimism is justified by fact that contamination is *on* the surface,
- And solar wind is *below* the surface.
- The separation between dirt and signal is small (typically 100A).
- But, being a sample return mission, all of contemporary science and technology is available to clean the surfaces without disturbing the implanted solar wind.
- With some luck, major effect will be delay in results.



<u>GENESIS</u> **Specific Measurement Objectives** (prioritized). Prelaunch.

- (1) **O** isotopes.
- N isotopes in bulk solar wind. (2)
- (3) (4)
- Noble gas elements and isotopes. Noble gas elements and isotopes; regimes.
- (5) C isotopes.
- (6) C isotopes in different solar wind regimes.
- Mg,Ca,Ti,Cr,Ba isotopes. (7)
- **Key First Ionization Potential Elements** (8)
- (9) Mass 80-100 and 120-140 elemental abundance patterns.
- (10) Survey of solar-terrestrial isotopic differences.
- Noble gas and N, elements and isotopes for higher energy solar particles. (11)
- (12) Li/Be/B elemental and isotopic abundances.
- Radioactive nuclei in the solar wind. (13)
- (14) F abundance.
- Pt-group elemental abundances. (15)
- (16) Key s-process heavy elements.
- Heavy-light element comparisons. (17)
- Solar rare earth elements abundance pattern. (18)
- Comparison of solar and chondritic elemental abundances. (19)

Measurement of bulk solar wind except when noted.



Color-coded Science Assessment; updated 5/10

- Measurement can definitely be made
- Should be Possible
- Challenging; many of these are large area analyses.
- Very Challenging; all of these are large area analyses.
- Not Possible

The number of green elements continues to grow. There is no red.



<u>GENESIS</u> **Specific Measurement Objectives**

(prioritized)

- (1) O isotopes.
- N lsotopes in bulk solar wind. (2)
- (3) (4)
- Noble gas Elements and Isotopes. (He, Ne, Ar Kr, Xe) Noble gas Elements and Isotopes; regimes (He Ne Ar, Kr, Xe).
- (5) **C** Isotopes
- (6) C lsotopes in different solar wind regimes.
- Mg, Ca, Ti, Cr, Ba Isotopes. (7)
- Key FIP Elements (Na, Mg, Fe, Si, Ca, Cr, Ni, AI, C, N, O, etc) (8)
- (9) Mass 80-100 and 120-140 Elemental abundance patterns.
- (10) Survey of solar-terrestrial lsotopic differences.
- (11) Noble gas Elements and Isotopes: higher energy solar particles.
- Li/Be/B Elemental and Isotopic abundances. (12)
- Radioactive nuclei in the solar wind. (13)
- (14) F abundance.
- (15) Pt-group Elemental abundances.
- (16) Key s-process heavy Elements.
- (17) Heavy-light Element comparisons.
- Solar rare earth Elements abundance pattern. (18)
- **Comparison of solar and chondritic elemental abundances.** (19)



Summary (unchanged)

- The bar has been raised considerably, but nothing is red even after 3 years.
- The amount of green is growing. Good prospects for (Cr, Mn, Ni) from SRTRXRF and (Ca,Cr,Al) from RIMS/ SIMS or ICPMS. There is a significant amount of blue. We are optimistic that blue will turn to green.
- Significant progress since hitting bottom on 9/8/04, but pushing forward on a broad front.
- With some luck, the major effect will only be a delay in science.