



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

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Introduction

The following 13 slides are a Genesis Misson overview, common to all Progress Reports.



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.



The Genesis Payload

Canister and Collector Materials pre launch





Solar Wind Regimes

- Three different kinds ("regimes") of solar wind:
 - High speed (coronal hole) Genesis H array
 - Low speed ("interstream") Genesis L array
 - Coronal Mass Ejections Genesis E array.
- 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)

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



<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.



O Isotopes. Summary

• Additional details on analyses and results are in Genesis May 2010 semiannual progress report (www.paque.com/genesis);

• SiC quadrant 60001 was analyzed as a function of radius. The $\delta(180)$ varies because of concentrator mass fractionation, but all analyses are consistent with $\Delta(170) = -28.3 \pm 1.8$ permil.

 Concentrator mass fractionation corrections based on analyses of Ne in 60001 (Heber et al., in press *Meteoritics and Planetary Science* 2011). Well defined profiles of Ne fluence and ²⁰Ne / ²²Ne were obtained.

Modeled Concentrator Ne fractionation (Wiens, LANL) similar to measured but some quantitative differences remain.

Models predict very similar fractionations for Ne and O, so adopt measured Ne fractionations to correct MegaSIMS O data. Resulting solar wind O isotopic composition shown in following slide.



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 between Sun and solar wind.
 - 1998-2005: Slight evidence from in-situ spacecraft for fractionation, but error bars were very large.
 - 2007: Significant differences in solar-wind regimes for HeNeAr from GENESIS samples (see Heber et al LPSC 2008, abs 1779)
- Theory:
 - FIP-correleated elemental fractionation suggests no isotopic fractionation.
 - Large fractionations suggested by Bochsler (2000) Coulomb drag model (next slide).



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.



<u>GENESIS</u>

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

¹⁵N/¹⁴N in the solar system (slide from Marty et al, 2010)





N isotopes from Collector Array Diamond-like-C G. Huss, Hawaii, Cameca 1280 SIMS

- This is a much more difficult measurement than on Concentrator target samples because the N fluences are $\approx 20x$ lower.
- But even with larger error bars, in light of anomalous Minnesota result, important to have an ¹⁵N/¹⁴N ratio independent of concentrator.
- Gardened surface contamination dominates solar wind for depths less than about 400 A.
- Instrumental Background dominates solar wind for depths greater than about 1500 A.
- But region between 400 and 1500 A mostly solar wind for both ¹⁴N and ¹⁵N

Correct region below 400 and beyond 1500 using theoretical profile (C. Olinger, LANL)

Preliminary del $^{15}N = -320 \pm 100$ permil (1 sigma) consistent with concentrator data.



<u>GENESIS</u> N Isotopes in 60001 SiC Concentrator Target. Marty, Chaussidon; Nancy SIMS analysis



Solar wind ¹⁴N counting rate as a function of sputtering time (depth in sample) for 60001 (blue) compared with a flight spare control SiC (red)

As for O with the MegaSIMS, a small amount of cleaning by sputtering with low E Cs leads to enhanced signal/noise with loss of only a small amount of surface.

The depth of the solar wind 14N is close to that predicted for the Concentrator.

Figure at the center : isotopic variations of Ne (Heber et al.) and N, expressed as deviations (‰ and per amu) relative to isotopic ratios measured at zone 1 & 2 (errors are 1 σ). We assume that nitrogen isotopes follow a behaviour similar to those of neon and that there is no concentrator mass fractionation from the real solar wind ratios at zones 1 & 2, as observed for Ne. In the bottom table, the measured 15N/14N ratios are corrected for isotopic fractionation using the permil/amu fractionations from Ne The error-weighted average is then computed and the result is corrected for isotope discrimination of the ims 1280HR² using the standard SiC data. The final value of -407 permil relative to the terrestrial atmosphere is our best estimate for the SW N isotopic composition.



	dist/center mm	¹⁵ N/¹⁴N measured	2 σ	(¹⁵N/¹⁴N) corr fract.	2σ
Zone 1	19	2.143E-03	9.00E-05	2.143E-03	9.00E-05
Zone 2	19	2.116E-03	2.00E-05	2.116E-03	2.01E-05
Zone 3	11	2.126E-03	2.90E-05	2.103E-03	2.95E-05
Zone 4	7	2.158E-03	3.80E-05	2.117E-03	3.88E-05
			weight. average	2.114E-03	1.50E-05
			norm. Std ઠ¹⁵N	2.178E-03 -407	2.22E-05 6





Conclusions

From both the UCLA/Genesis MegaSIMS and the Nancy Cameca 1280 SIMS, the 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: additional 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. *Geochimica, Cosmochimica, Acta* 73, 7414, 2009.
- Heber et al. Isotopic and elemental fractionation of solar wind implanted in the Genesis concentrator target characterized and quantified by noble gases. In press, Meteoritics and Planetary Science, 2011.



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.



Isotopic fractionation of solar wind and atmospheric Kr Meshik and Hohenberg, Wash U.



Superposition of Genesis polished AI (PAC) data (red points) on literature compilation of measurements of lunar regolith 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.

FIG. 13. As in Fig. 12, for total or fractional Kr & ases from the listed samples. Data solices reference in Table 4. Spallogenic Kr components are considered to be negligible in eight of these fourteen compositions, and small (except for etch fractions 3-4 and 3-10 from 79035 illmenite) in the others. Plotted errors for this latter group do not include appears to be simply mass the generally minor effects of uncertainties in relative spallation yields (Table 4D).


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 provides 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. This has been eliminated in most recent analyses.



Xe isotopic composition Crowther and Gilmour, U. Manchester

RELAX = refrigerator enhanced 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 uv laser step heating.
- Atoms from many pulses trapped at 80K; released in single IR laser pulse.
- Released atoms ionized with uv laser.
- 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 30 pulses mostly solar wind
- Non flight samples give background Xe in Si.



Relax Summary, con't

- Observe variable concentrations of Xe in both flight and nonflight samples.
- Mixing line approach provides basis for deriving SW Xe isotopic composition.
 - Data consistent with mixture of atmospheric Xe and solar wind.
 - Plot isotope ratio vs (1/ ¹³²Xe)
 - Extrapolate to known solar wind ¹³²Xe from Heber et al to get solar wind isotopic composition (following slide).
 - Possible differences from young lunar regolith samples for ¹³⁴Xe, ¹³⁶Xe.
- Additional discussion in May semi-annual (www.paque.com/genesis)



Young lunar regolith: 71501 ilmenite – Wieler & Baur 1994, Pepin et al. 1995



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

This and following four slides are background used in previous reports.

- 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 by factor of 2-3.
- 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 potential, solar wind and photosphere isotope ratios expected to be same.



Fractionation Factor

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



FIP Plot from spacecraft data





Parameters used to characterize solar wind-photosphere element fractionation. (Wiens et al., LPSC 2010)

- First ionization potential (FIP)s
 - High FIP elements depleted by ~2x relative to low FIP elements in interstream (L array) wind. Relatively little fractionation in coronal hole (H array) 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.



<u>GENESIS</u>

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





Noble Gas Elemental Abundances

These were summarized in May 2010 semiannual report (<u>www.paque.com/genesis</u>), based on Heber et al (2009) and Vogel et al (LPSC 2010).



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

- Sample sputtered with O2+ ions, in presence of O₂ flood gas for Si.
- Analyses at ASU (Jurewicz, Guan, Hervig), UCLA (McKeegan, Heber), CIW (Wang, Nittler), and Caltech (Heber, Guan, Jurewicz)
 - 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.
- Many 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.

Improved method of implant fluence calibration.

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

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 26.5 ppm Mg. Accurate measurement of our 617 sample by isotopic dilution (Humayun, FSU).

Nominal Srni IV 25Mg implant fluence = 3e13/cm^{2.}

Except for small (< 0.1%) 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.

The average measured fluence based on two profiles each for the three 617 samples gives a CZ4A fluence of 2.81x10¹³/cm² with a one sigma standard deviation of 1.5%.

Using CZ4A, accurate SIMS intercalibration of the K7A implant used for flight sample analysis in progress. Intercalibration should be accurate to better than 2%. With luck, final Genesis Fe/Mg will be reported at 2011 LPSC.

Solar Wind N fluence from 60001 Concentator SiC. (Chaussidon and Marty, Nancy)

N fluences were computed based on an ¹⁵N implant. Uncertainties were estimated from reproducibilities of standard SiC measurements. For Zones 1 & 2, a mean value of the two determinations was taken. The center figure shows that the N fluences increase as expected with distance and track the ²⁰Ne fluences of Heber et al., 2011. The table shows that N/Ne is constant consistent with the concentrator models of Wiens. The mean ²⁰Ne/¹⁴N ratio of all 3 zones is 0.87±0.23, similar within errors to the estimate of the (²⁰Ne/¹⁴N)_{SW} of 1.14±0.23 (Marty et al. 2010).

Using the accurate bulk solar wind fluence of 1.26x1012 (Heber et al., 2009), a bulk solar wind N fluence of 1.1x1012/cm2 is obtained.

Synthesis : abundance



Distance from concentrator's center, mm

	dist/center	¹⁴ N	1σ	²⁰ Ne/ ¹⁴ N	1σ
	mm	at/cm ²			
Zone 2	19	2.50E+13	5.07E+12	0.86	0.20
Zone 3	11	4.40E+13	8.94E+12	0.87	0.20
Zone 4	7	5.40E+13	1.10E+13	0.89	0.20



N Fluence from Collector Array DLC G Huss; Hawaii, Cameca 1280 SIMS

- Gardened surface contamination dominates solar wind for depths less than about 400 A.
- Instrumental Background dominates solar wind for depths greater than about 1500 A.
- But region between 400 and 1500 A mostly solar wind for ¹⁴N.
- Correct region below 400 and beyond 1500 using theoretical profile (C. Olinger, LANL)
- Preliminary N bulk solar wind fluence 1.6e12/cm², a bit higher than the Nancy result.

Bulk solar wind O, C fluences Heber, Woolum, S Smith(EAG), McKeegan, Kallio, Jurewicz, Guan



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, was still 10x the solar wind.



Fall 2009. Caltech 7f Major Improvements



Instrumental Background reduced by:

- 1e-10 Vacuum
- Many days of pumpdown
- Overnight Si sputtering.

Surface Contamination reduced by:

Low E (5 keV) Cs surface cleaning.

Solar wind measured between 500 and 2000A, but surface bkg. still too high

Solution: Back Side Depth Profiling

Sample preparation (EAG)

- Epoxy up-side-down onto Si Substrate.
- Grind + polish to 0.4 2 microns thick
- B/C array Si fragments (5-8 mm)
- Fringes: sample is flat only in the center part

30722



Depth profile: sputtering from the back side of the thinned sample.

- > no gardened surface contamination
- good measurement of instrumental background
- > analysis of almost complete SW profile
- > no transient sputter effects during SW profile

See Heber et al LPSC10 and MetSoc2010 abstracts

Backside Depth Profiling Samples

60757 0.35 microns thick

30767 2.1 microns thick

Genesis backside depth profiling analysis in 3 steps

- (a) $125 \times 125 \mu m^2$, 30nA beam \rightarrow remove surface contamination (¹²C, ¹⁶O, ²⁸Si)
- (b) $100 \times 100 \mu m^2$, 10nA beam \rightarrow Si count rate, (¹²C, ¹⁶O, ²⁸Si)
- (c) $100 \times 100 \mu m^2$, 10nA beam \rightarrow to increase data coverage for SW profile ¹²C, and/or ¹⁶O measured; Si count rate from (2) was assumed to be constant



¹²C depth profile for 60757

30767 profile 7: Optimize spatial, depth resolution to get as close to surface as possible



- 5 keV impact E
- Smallest field aperture.
- 30% gating
- Low sputtering rate
- Accept penalties in analysis time and counting rate.

3D projection of interferometer profilometry (UCLA)

CNO Fluences: status

- Have good profiles for C, O, and N from two SIMS instruments:
 - Cameca 7f CalTech
 - EAG Quad SIMS (Smith)
- Good C profiles for both samples. N data for 60757.
- O tends to break through earlier on thinner 60757. Data from thick 30767 are better.

Final data processing in progress; will be presented at 2011 LPSC.

Preliminary Bulk Solar Wind Fluences:

C: 6.5e12/cm2 O: 1.1e13/cm2



Resonance Ionization Mass Spectrometry (RIMS) essentials. ANL Veryovkin et al.

- 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.

Three element RIMS analysis:

422.79 nm, 369.635 nm and 285.296 nm light

Simultaneously detect Mg, Ca and Cr using only three tunable lasers





RIMS upgrades

A major instrument upgrade has been carried out 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 (500eV) 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 retains higher energy to provide adequate sputtering rate.



(2) Improved discrimination against surface contamination



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.

Improved spatial resolution can also be achieved by rastering the pulsed beam, and accepting counts only near the center of the raster (gating).



Bulk SW Mg depth profile in 60178 Si; atoms ²⁴Mg/cc



Background correction based on observed signal beyond 300 nm.

Good agreement with theoretical depth profile (Chad) between 40 and 300 nm.

Some residual surface contamination below 30 nm



RIMS-SIMS fluence comparisons

Element	RIMS	SIMS
Mg	2.24e12	2.15e12 ASU 6f
Са	9.4e10	1.0e11 UCLA 1270
Cr	3.3e10	3.0e10 UCLA 1270

All data preliminary, but agreement good at this point.

Total Reflection X-ray Fluorescence (TRXRF) B King, M Gladys (Newcastle) C. Glover (Australian synchrotron)

XAS beamline at Australian Synchrotron

- 7.5, 10, 14, 17keV X-ray energies
- beam size 0.17mm (H) x 0.3mm (W)
- beam divergence 10⁻⁴ (V) and 5x10⁻⁴ (H)
- flux 10¹² photons s⁻¹
- 100 element Ge detector
 - mounted horizontally normal to the x-ray beam
 - count time 60-600 s
- Sapphire (Al₂O₃) samples
 - approx 1cm square, 0.7mm thick, mounted horizontally on Perspex
 - Genesis flight sample 60642 from NASA "lending library"
 - identical sample which did not fly on spacecraft
 - standard implanted with 2x10¹³ cm^{-2 54}Fe at 168keV
 - no special preparation

TRXRF has previously been successfully used for Genesis samples Kitts et al., *J. Appl. Physics* **105**, 64905, 2009

Reflectivity measurements





In principle, deconvolution of the angular scans can resolve a surface contamination component from implanted solar wind for abundances of 1st row transition elements (Ca – Zn). Additional beam time for Genesis analysis has been approved for 2011.



<u>GENESIS</u>

FIT plot from Genesis data

- We can compile the noble gas fluences (Heber et al., 2009) with the Mg and Fe fluences (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, along with N fluences from this work.
- 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.

Radioactive Nuclei in the Solar Wind (¹⁰Be, ²⁶Al, ⁵³Mn) K. Nishiizumi, A. Bixler UCB SSR



~8,000 cm² of Mo coating (~300 nm) on Pt (~48 µm)

All foils have Utah soil contamination on the surface, but the amount is highly variable. This is the most challenging of all Genesis analyses.

Minimum requirement for decontamination of Utah dirt <1 mg Be over 8,000 cm² surface or <10003g/cm²



Development of surface cleaning

Test more than 70 reagents using more than 1,600 foils by March 2010

Major problem: Mo coating has high solubility, even in water because of high degree of oxidation.

Solution: Reduce MoO₃ with H₂ at elevated pressure and temperature.



H₂ Hydrogenation



H₂ produces big decreases in amount of Mo removal by H₂O (60min)



Solvents plus chelating agents preferentially remove dirt.





SEM Study of Cleaned Mo on Pt Flight Samples

Samples shown were treated at 1600 PSI H2 and 85C for 2 days before THF treatment







40391,0133

SEM X-ray spectra of 0123 shows no dirt. Cleaning works well for this sample. More work needed for heavily-caked samples like 0133.



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 catalogs at a high level of completion, 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.

Following 10 pages are background on sample cleaning included with all Progress Reports.



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 approaches 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 is 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, Australia) and TOFSIMS (Manchester) have adequate sensitivity.
 - Genesis time for SRTRXRF 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 10⁹- 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 lab TRXRF spectra for the same spot on sapphire sample 60242. Overall we have TRXRF data on 30 samples and controls, most analyzed multiple times.

As shown for 60242 we have had good results with simple dilute HCI cleaning but there are also several recalcitrant samples that are resistant to HCI cleaning. Sapphire 50719 is discussed as an example below.

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. For many, but not all, samples it has been possible to remove the Ge as illustrated in the after HCl cleaning spectrum for 60242.

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. It is not seen on Si control samples.



After HCI Cleaning



Australian SR-TXRF Spectrum

SR-TXRF 600s count time



Sapphire flight spare control sample 1898. Clean to laboratory TRXRF.

Analysis at peak reflectivity; preferentially sampling surface contamination. Many elements detected.

This is somewhat disappointing as flight samples expected to more difficult to clean.

Acid cleaning needs to be improved. Tests under way with more vigorous attack.

Si from flight SoS found to be unexpectedly soluble in HF (Humayun) whereas control samples are insoluble. Acid treatments will have to be checked with SIMS against small flight Si samples. The present HCI treatment was shown to cause negligible erosion by analyzing solar wind H in Si, which is a very shallow implant.

Australian SR-TRXRF: relative levels of Fe surface contamination on three Genesis sapphire samples

Fe cps below critical angle (0.2 degree) reflects surface contamination. Both control 1898 ("non-flight") and "Genesis" flight (60242; previous slldes) have been acid cleaned. 60242 has less surface contamination of Fe than 1898 and implant samples.

Additional cleaning will be done of these samples before next Australian synchrotron run in 2011.





Optical Microscopy of sapphire 50719. (Jurewicz, ASU)



Reflected and transmitted light images of metal smears on 50719.

The smears will be mapped, and a portion of the sample C coated for SEM study to identify the smears. The uncoated parts will be used to find an etchant that removes the smears. The initial post JSC uv-ozone TRXRF spectrum for sapphire sample 50719 showed large Ge, Si, S, and Ca peaks. Two acid treatments removed all but the Ge and Si peaks, which remained relatively large.

Optical microscopy of 50719 showed the presence of large numbers of hundreds of micron size metal(?) smears. These are likely HCI-insoluble Si metal possibly with some trapped Ge. The Ge and Si are both pure collector materials, but other contaminants may have been trapped in the deposits but at levels not detectable with lab TRXRF.



<u>GENESIS</u>

Cleaning Summary

As of Dec 1, 2010, we are well into the TRXRF study. There has been enough success with HCI cleaning that this is the main acid of choice at present, but improvements are required.

All samples analyzed been treated in a standard manner: uvozone(JSC) → dilute HF (Caltech; removes SiO2 from brown stain silicones) → HCI (CalTech) → TRXRF.

Cleaning of SoS with supercritical CO_2 at JPL was not especially successful. Additional stainless steel contamination from the apparatus was added, which has been surprisingly difficult to remove, requiring 1:1 HCl treatment. There is some suggestion of surface roughening with the 1;1 HCl. This does not occur with flight spare control Si, but flight SoS is known to be more reactive.

ANL has set up a system for CO₂ snow cleaning, but systematic cleaning tests have yet to occur.



<u>GENESIS</u>

Cleaning Summary, con't

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 additional SIMS checks of SW H profiles, where the profile is well known, will be made. Additional solar wind H fluence data is a byproduct of these tests.

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.



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.
- (18) Solar rare earth Elements abundance pattern.
- **Comparison of solar and chondritic elemental abundances.** (19)



Summary (essentially unchanged)

- The bar has been raised considerably, but nothing is red even after 6 years.
- The amount of green is growing. Good prospects remain for (Cr, Mn, Ni) from SRTRXRF. 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.