GENESIS

SEARCH FOR ORIGINS

Status and Science Results

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GPMC, May 2009

Contents

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.

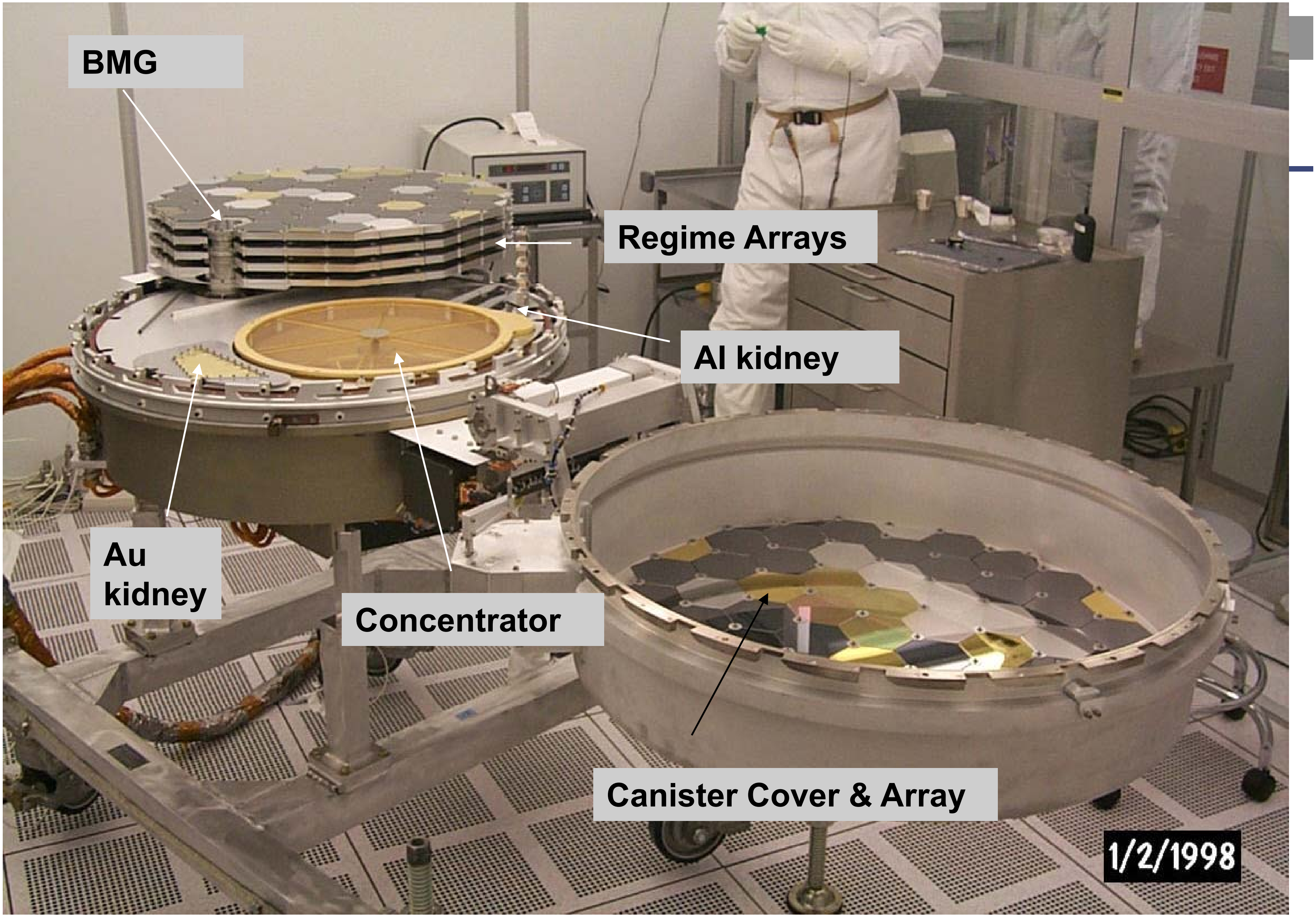
- Returned materials to Earth for analysis in terrestrial laboratories.

Why: Genesis Science Objectives

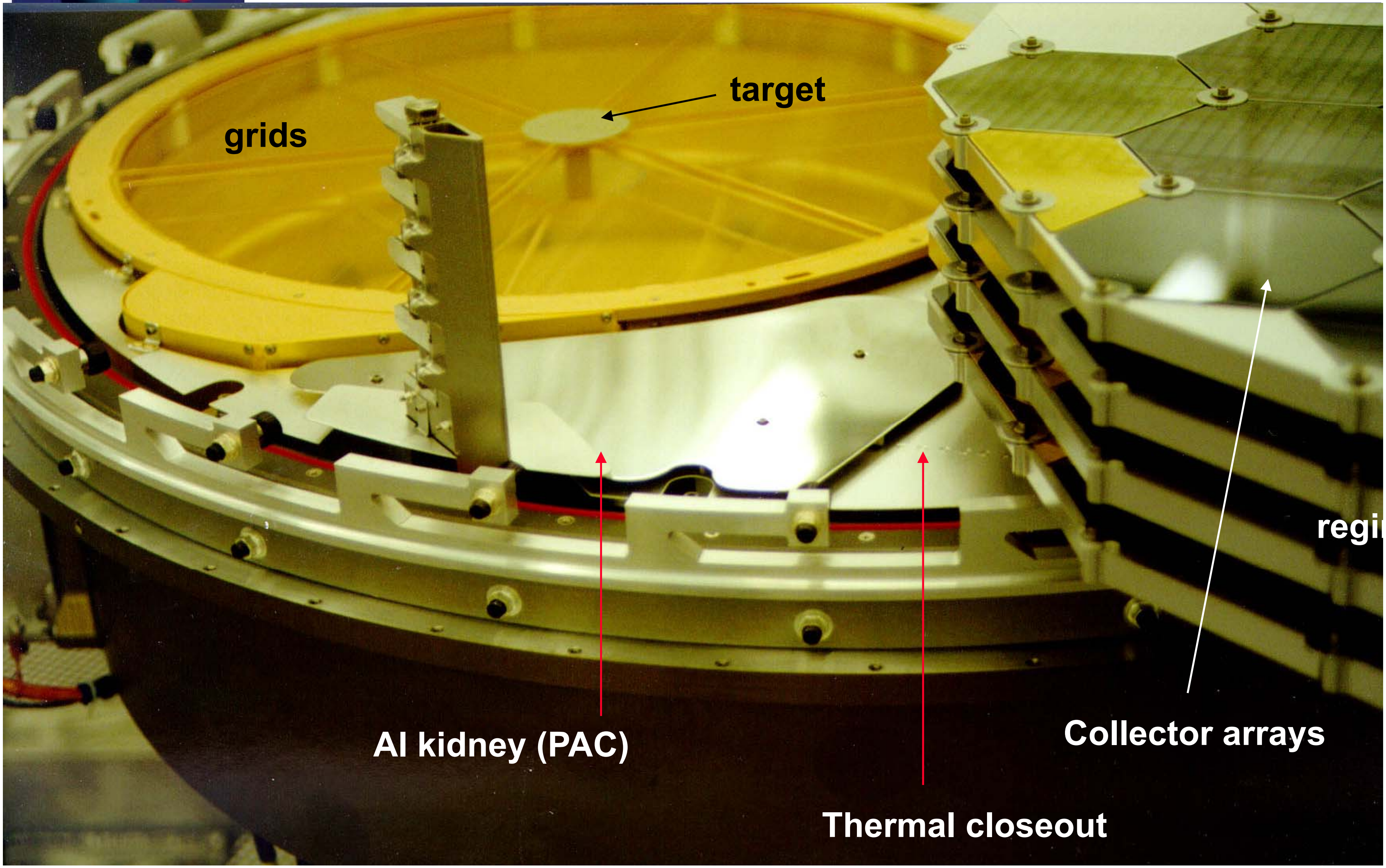
- Provide solar isotopic abundances to level of precision required for planetary science purposes.
- Provide greatly improved knowledge of solar elemental abundances.
- Provide a reservoir of solar matter to meet the needs of 21st century planetary science.
- Provide elemental and isotopic data for the 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


BMG
Regime Arrays
Al kidney
Au kidney
Concentrator
Canister Cover & Array
1/2/1998

Canister and Collector Materials pre launch



Analysis Overview

- Genesis sample analysis/testing is proceeding on a broad front in 28 laboratories worldwide.
- Rates vary, but progress is being made.
- 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.

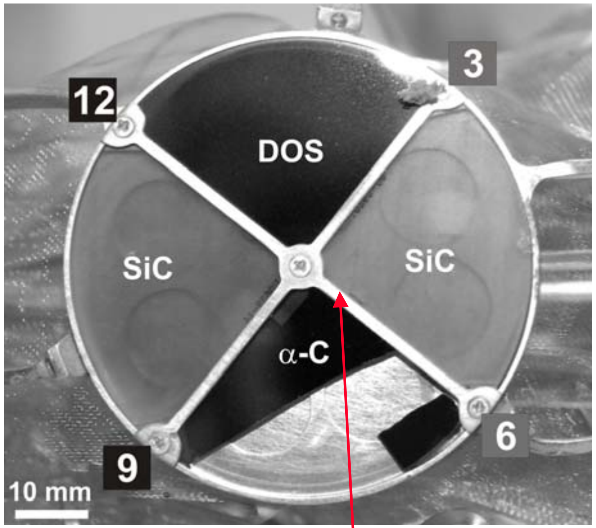
Mass spectrometry is the most widely-used analysis technique.

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 (HNO_3, 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
- Accelerator *Mass Spectrometry*
  - – Extraction by differential chemical etching.
- Radiochemical Neutron Activation Analysis
  - – Extraction by differential chemical etching.

In-flight Concentrator Performance from analysis of Au cross. (V. Heber et al; LPSC 2009 abstract)

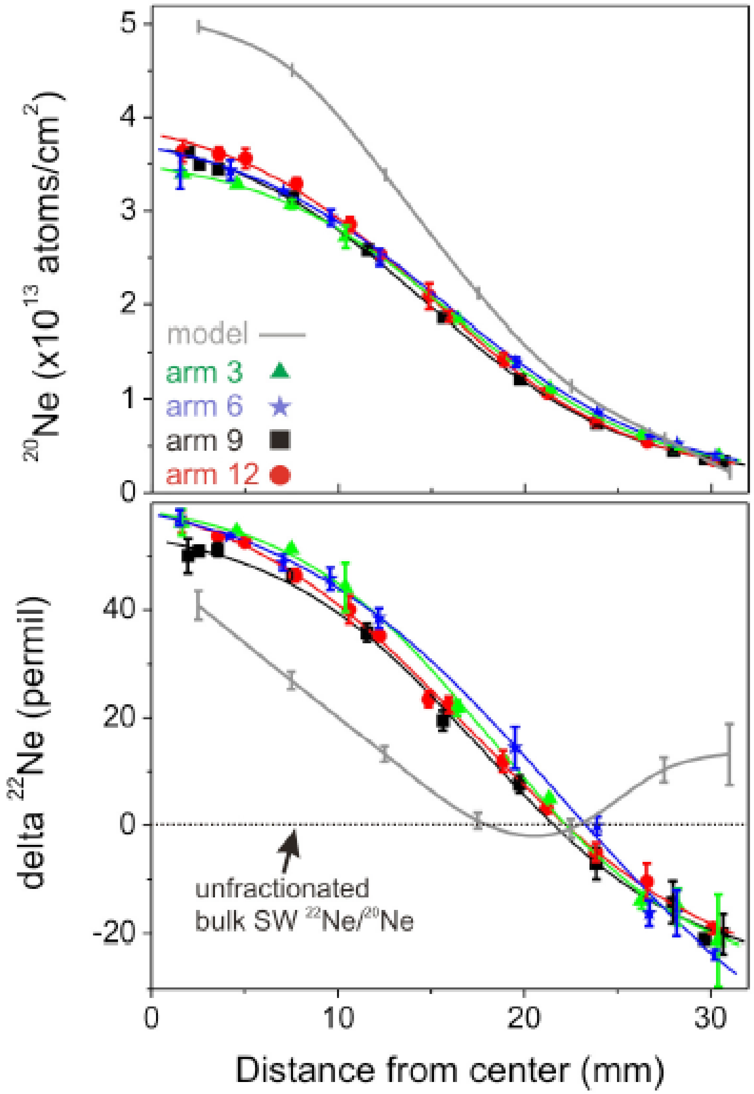
Recovered Targets and Holder



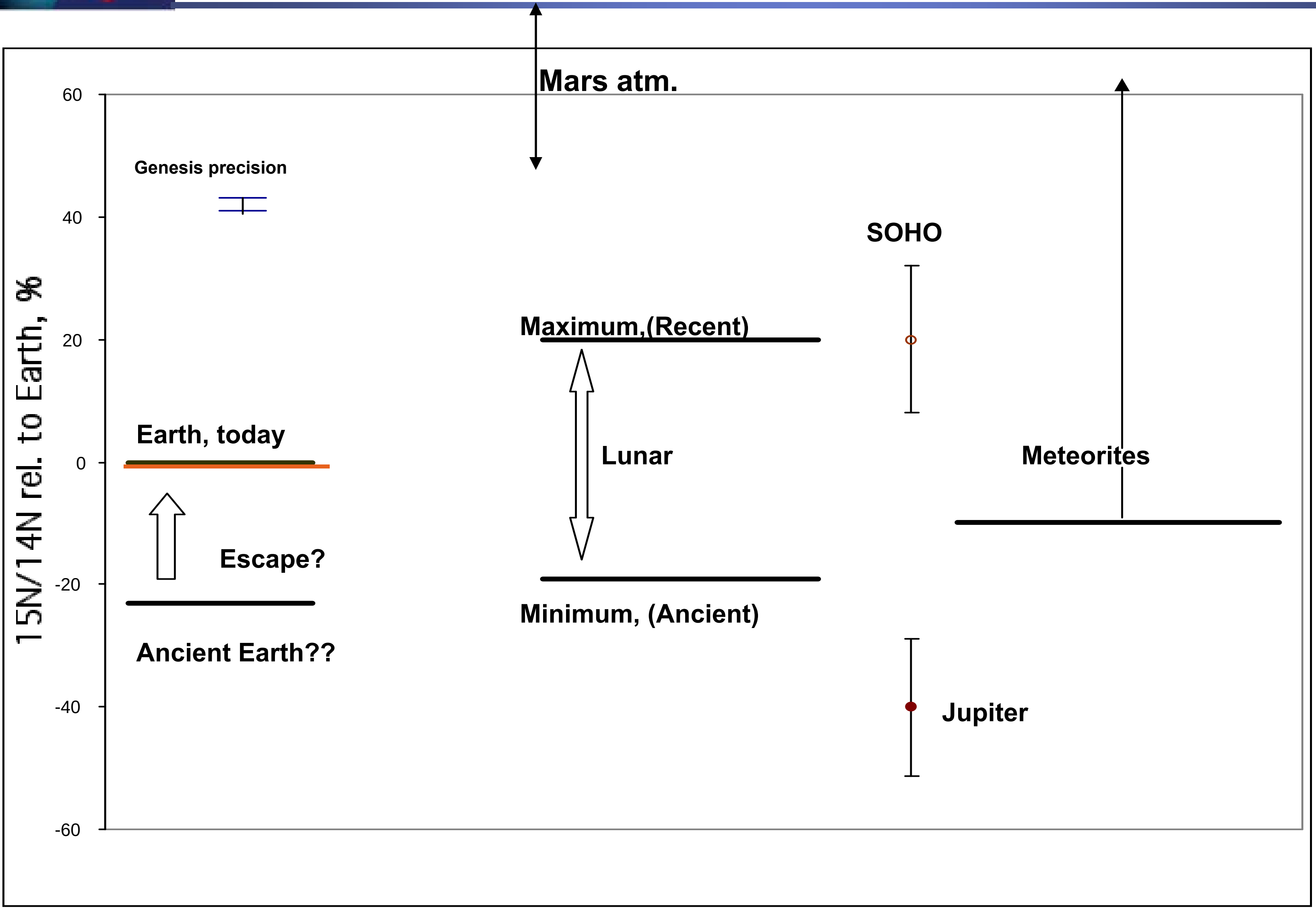
Au cross held targets in place

Ne can be measured on 100 micron size spots by laser ablation.

Data for all 4 arms agree. Very important: no azimuthal SW inhomogeneities in targets.

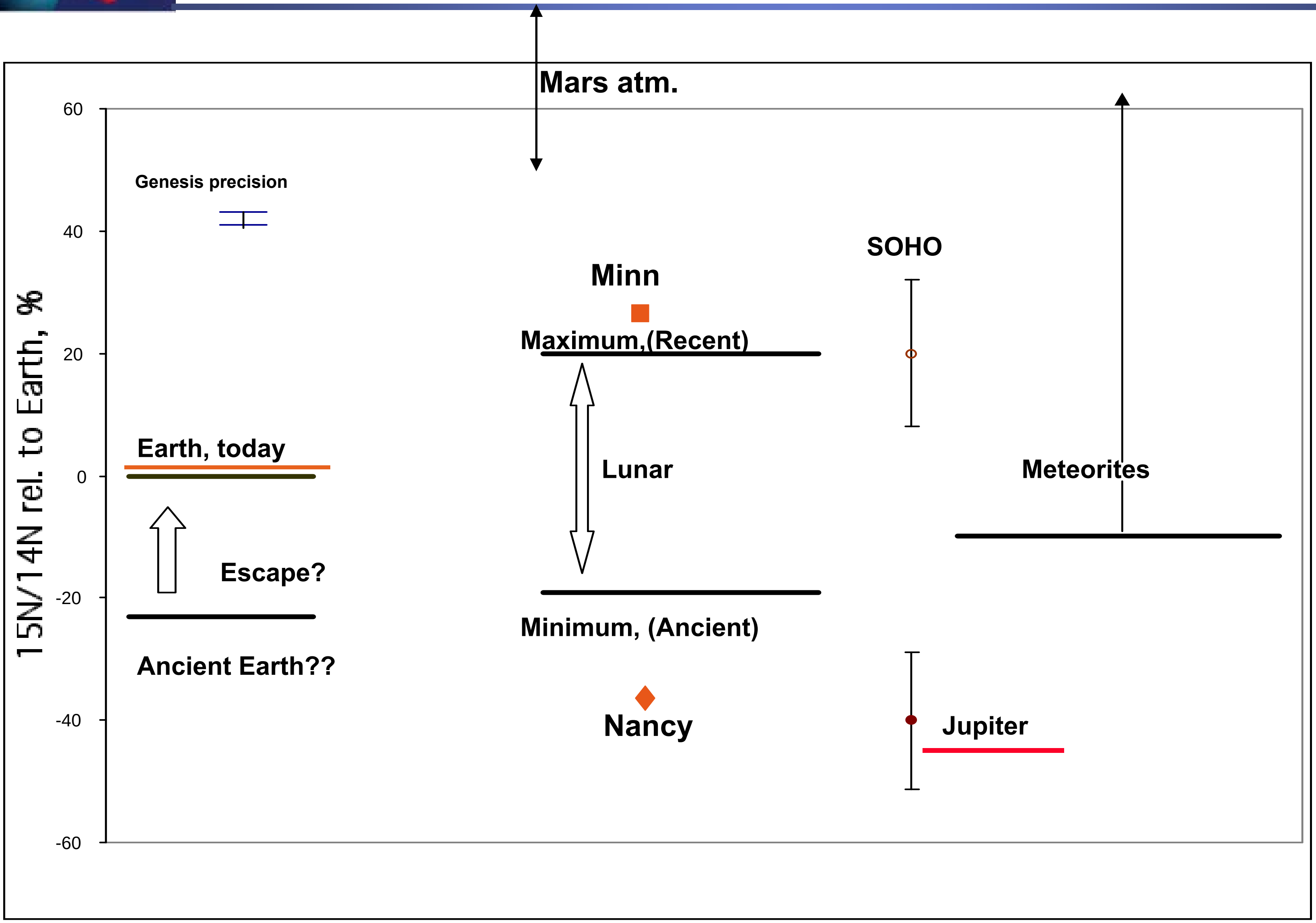


The isotopic composition of N shows wide variations in solar system materials. This is our #2 Science Objective



N isotope analysis status

- **Samples have been allocated to two laboratories:**
  - **U. Minn**
    - **Release and analysis of N_2 by room temperature amalgamation of AuoS collectors.**
  - **CRPG Nancy, France**
    - **Laser ablation depth profiling with analysis of N_2**
    - **data based "Au cross" frame from Concentrator target holder (slide 11).**
- **Distinctly different analysis techniques are being used, so if consistent results can be obtained, great confidence can be attached to the results.**
  - **However, at present, there is a discrepancy in the results from the two laboratories.**


Mars atm.
60
40
20
0
-20
-40
-60
15N/14N rel. to Earth, %
Genesis precision
Earth, today
Escape?
Ancient Earth??
Minn
Maximum,(Recent)
Lunar
Minimum, (Ancient)
Nancy
SOHO
Jupiter
Meteorites

Plan B for N

- Analyses at both Nancy and, to a lesser extent, Minnesota have been limited by high amounts of N impurities in Au collector materials.
- This possibility was anticipated in mission planning, and 1/4 quadrants in Concentrator target contained a Sandia diamond-like-C (DOS) sample from which N should be analyzable by stepwise combustion or possibly by SIMS.
  - This quadrant was broken in the crash, but most pieces have been recovered (see Alton et al LPSC 09 abstract).
- Stepwise combustion efforts are underway at Open U (England) and U. Minnesota.

Plan B for N, con't

SIMS isotopic analyses in collector array Si and DOS samples have failed.

- With the indication of Jupiter-like N in the revised Nancy data, it was important to try. SIMS sensitivity is adequate.
- Impact mixing effects prevent SIMS solar wind N analysis in the first 500 A; instrumental background dominates at depths beyond 1500A, but for 500-1500 A solar wind dominates under good vacuum conditions of CalTech 7f instrument.
- Distinguishing between terrestrial and Jupiter-like N potentially feasible.
- With Si, 15N measured as 28Si15N$^+$ at mass 43, but much larger amounts of 29Si14N cannot be mass-resolved.
- Measurement from DOS should be feasible, as 12C15N$^-$ is resolvable from all known interferences, but a surface-correlated interference of unknown origin is present, even on control samples.
  - The samples have been kept in high vacuum for many months, and a second attempt will be made in the next quarter.
- Problems encountered with the 7f should be much less using the UCLA MegaSIMS and using concentrator SiC.
  - This requires learning to deal with the increased energy spread of N+ ions from the breakeup of the CN$^-$ ions in the accelerator.

Heavy noble gas analyses on the Polished Al Kidney (PAC) Wash U

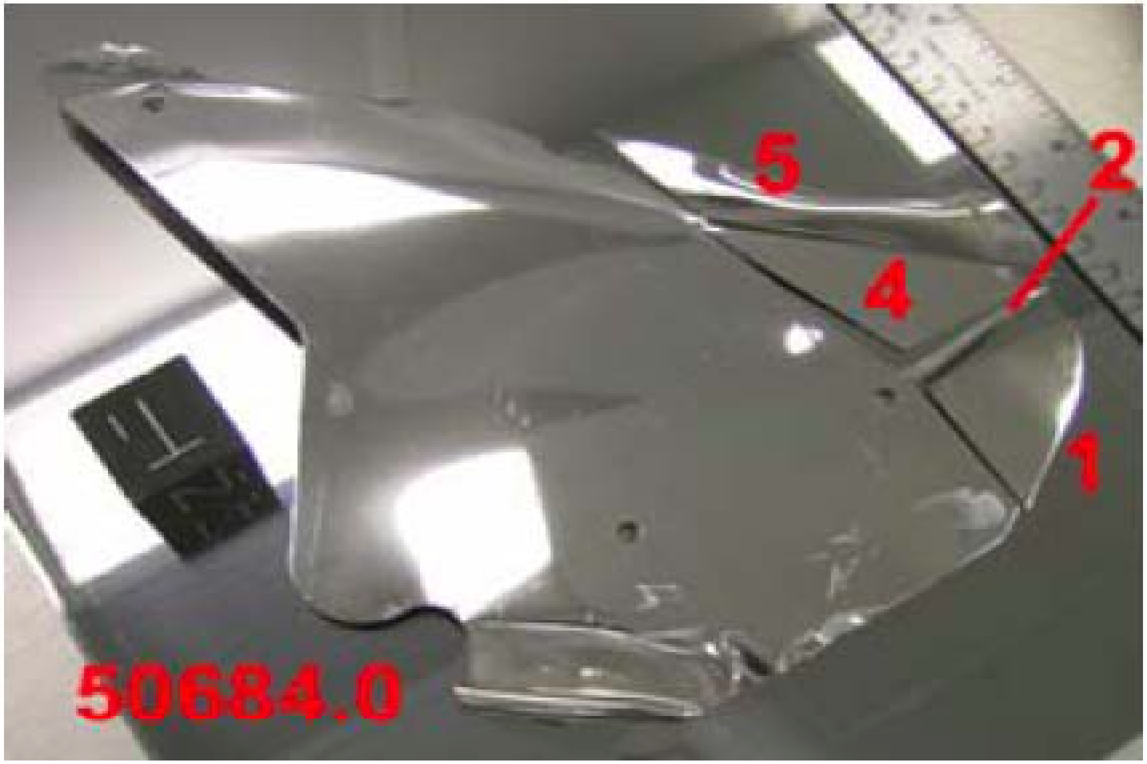
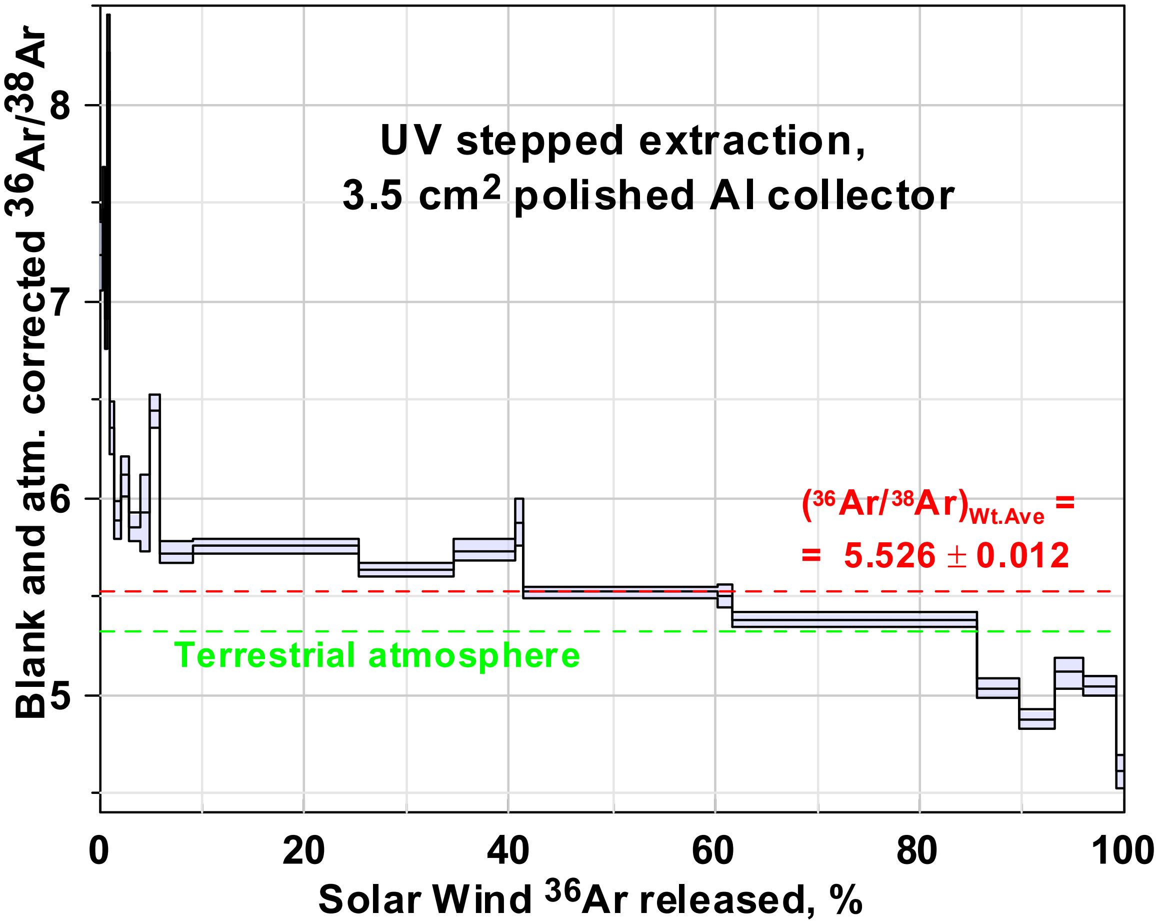


Fig. 1. "Kidney" collector after initial subdivision.

Cube is 1 cm in size.

This large piece of polished Al was added to the part of the canister surface exposed to the solar wind once the collector arrays were deployed. (See slides 6 and 7). The anticipated use was to provide large area samples for heavy noble gas (Ar, Kr, Xe) analysis. Prelaunch blanks of bulk samples indicated that if a thickness of less than 0.5 micron were analyzed, the levels of ArKrXe contamination were not significant compared to the solar wind.

Ar Kr Xe analyses (Wash U) Meshik et al LPSC



Simultaneous measurement of the two Ar isotopes gives high precision isotopic ratios.
The instrument can measure up to 8 isotopes simultaneously.

The power level of a uv ablation laser was adjusted to remove only a small amount from the surface, and the solar wind Ar isotopic composition measured with each step in the release.

The decreasing $^{36}Ar/^{38}Ar$ ratio results from isotopic fractionation during implantation and is expected.
The average is different from the Earth, as reported previously.

The successful SW Ar depth profiling points the way for similar experiments on Kr and Xe which will minimize the effects of surface contamination.

Meshik et al LPSC 09: Kr depth profile

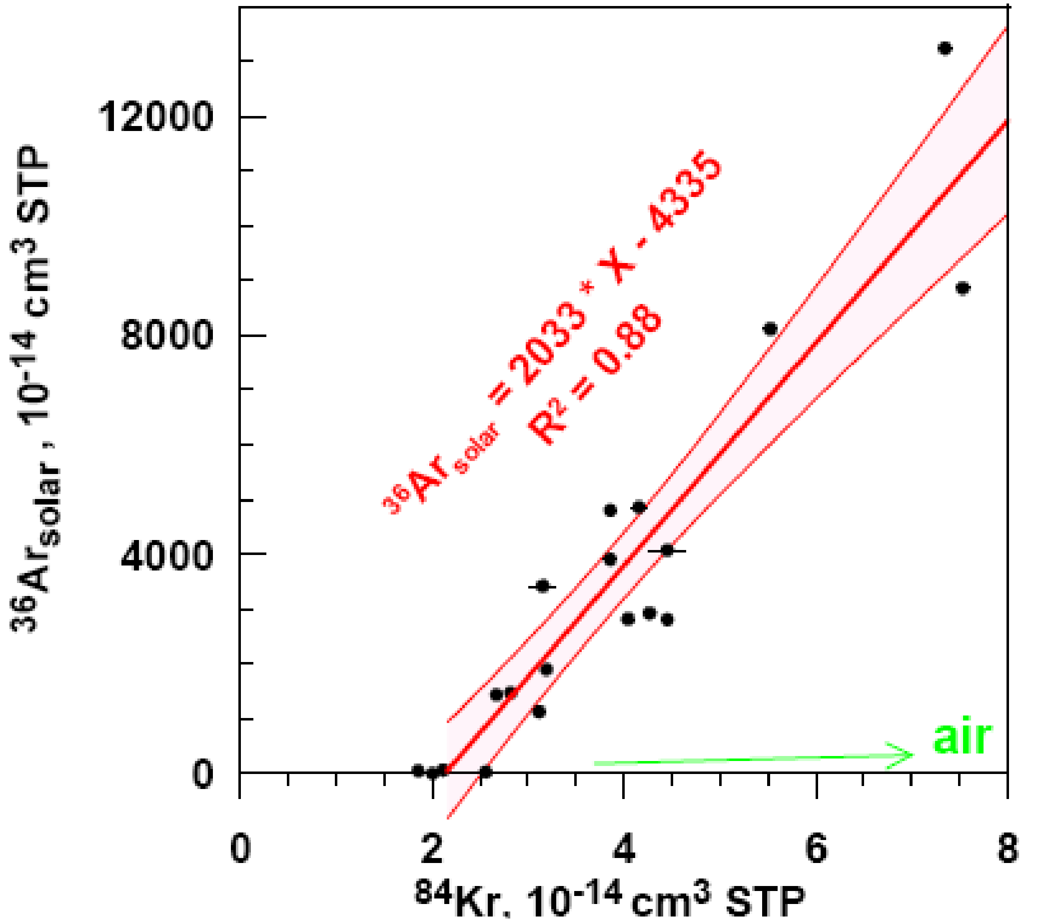
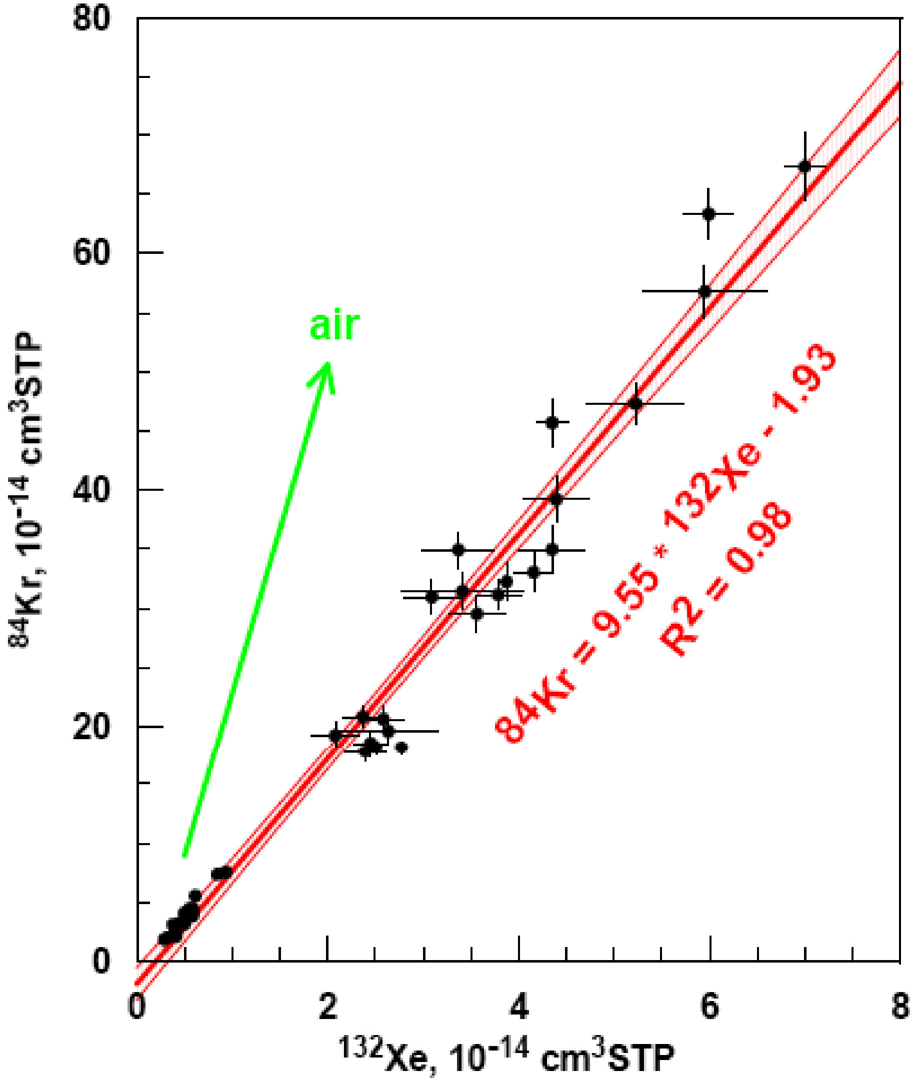


Fig. 2. Solar wind ^{36}Ar and ^{84}Kr from stepped power UV laser rasters of 0.34 cm^2 and 0.16 cm^2 areas of the PAC. Differences in implantation depths contribute to the spread from linear.

Individual points represent steps in laser ablation depth profile, as shown in previous slide.

Constant ^{36}Ar/^{84}Kr ratio not expected as Kr depth profile deeper. Earliest steps with low ^{36}Ar/^{84}Kr represent air surface contamination.

Meshik et al LPSC 09: Xe depth profile



Individual points represent steps in laser ablation depth profile.

The ^{84}Kr and ^{132}Xe depth profiles are sufficiently simukar

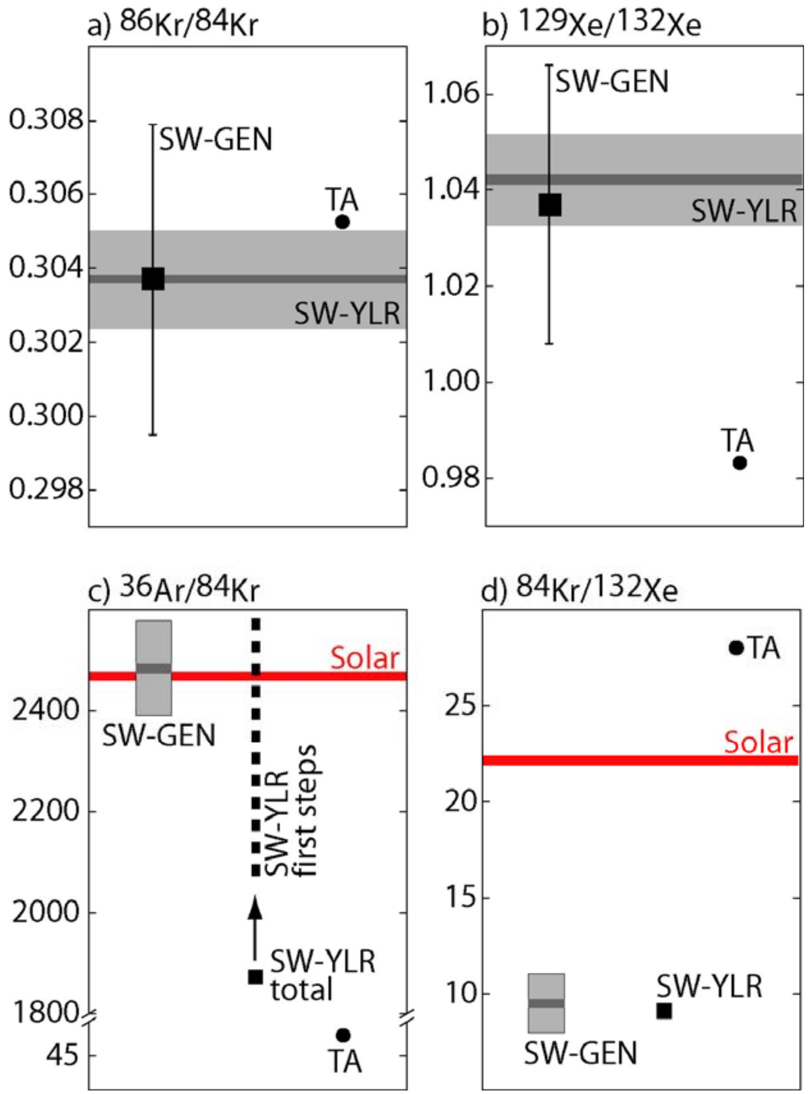
As was previously known from meteorite studies, the solar wind Kr/Xe ratio is much less than that in the terrestrial atmosphere.

Blank corrections on the data are still required, but a firm constraint is that:

$$^{84}\text{Kr}/^{132}\text{Xe} \leq 9.71$$

There are no true photospheric abundances for noble gases. The Anders & Grevesse abundance compilation gives ^{84}Kr/^{132}Xe = 20.7. The difference would be consistent with FIP fractionation, but this would be larger than expected.

Vogel et al (ETH Zurich) LPSC 09



Single step laser ablation analyses of bulk solar wind ArKrXe from CZ Si.

Results are compared with closed system etching data of lunar ilmenite (YLR) from a lunar sample of low cosmic ray exposure age, with the terrestrial atmosphere (TA), and with estimates from "solar" abundance compilations. (There are no photospheric abundance data for noble gases).

These Genesis data agree with those from Wash U on previous page. Terrestrial atmospheric noble gas data have long been recognized as not representative.

Except for ^{36}Ar/^{84}Kr, the Genesis and lunar regolith data agree, but alternative interpretations of the ilmenite etch data for ^{36}Ar/^{84}Kr (dotted line) are possible.

If the ^{84}Kr/^{132}Xe Genesis- "solar" differences were a FIP effect, then a similar difference in ^{36}Ar/^{84}Kr would be expected. We may be into "physics beyond FIP"

Xe isotopic composition
Crowther and Gilmour, U. Manchester

RELAX = resonance ionization mass spectrometric analysis of Xe.

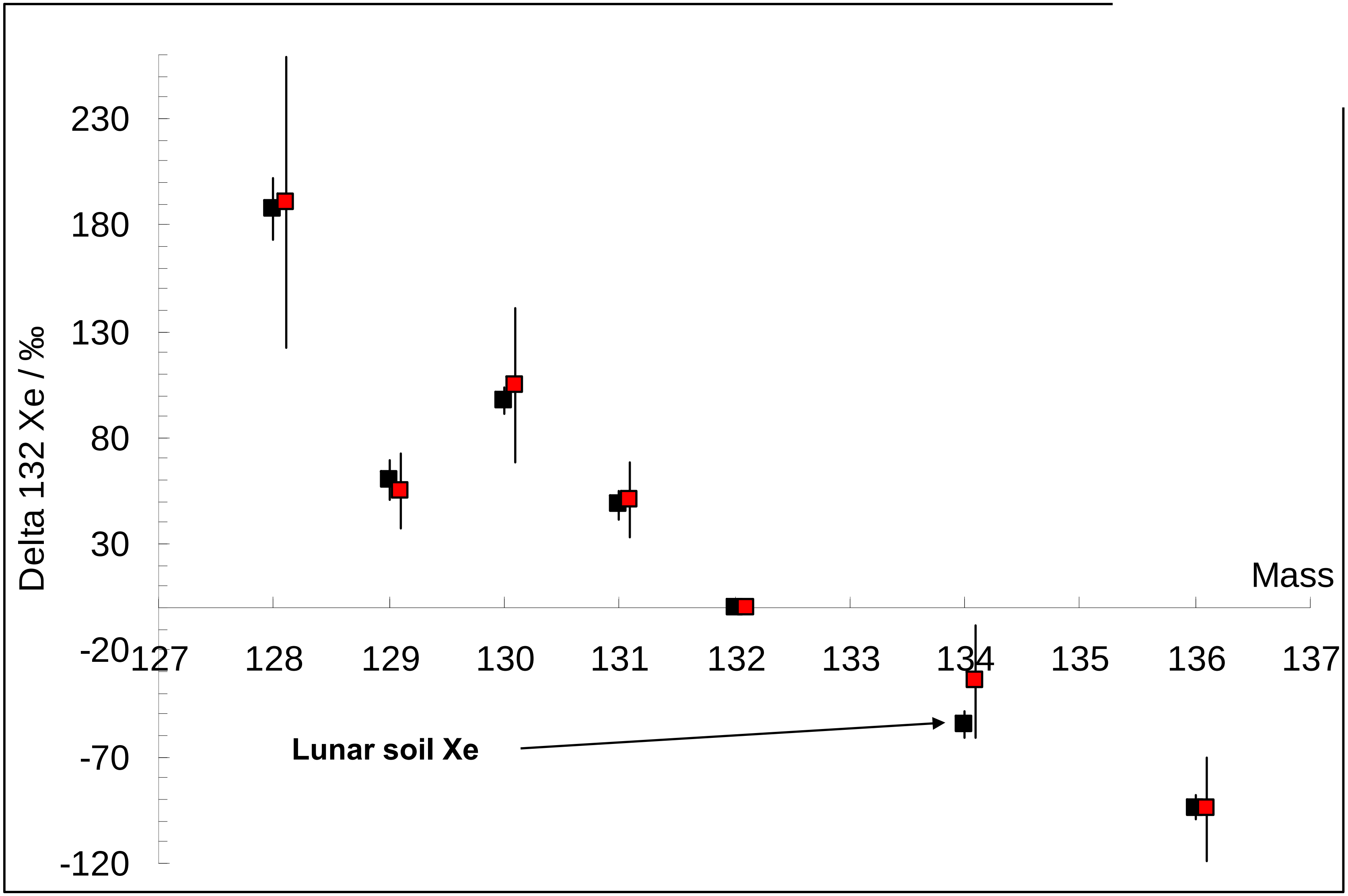
Exceptional sensitivity: 1000 atom detection limit.

Previous data (see 5/08 GPMC) based on IR laser heating.

UV laser ablation depth profiling offers better discrimination of solar wind □Xe from Xe impurities in Si collectors and surface contamination Xe.

- Low power UV ablation successfully extracts implanted solar wind
  - Power density < 700 mJ cm^{-2}
- High powers
  - “Dig” too deep
  - Also extract Xe intrinsic to Si

CZ 60480 4x5 mm sample; 1.2x10^5 Xe atoms.



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

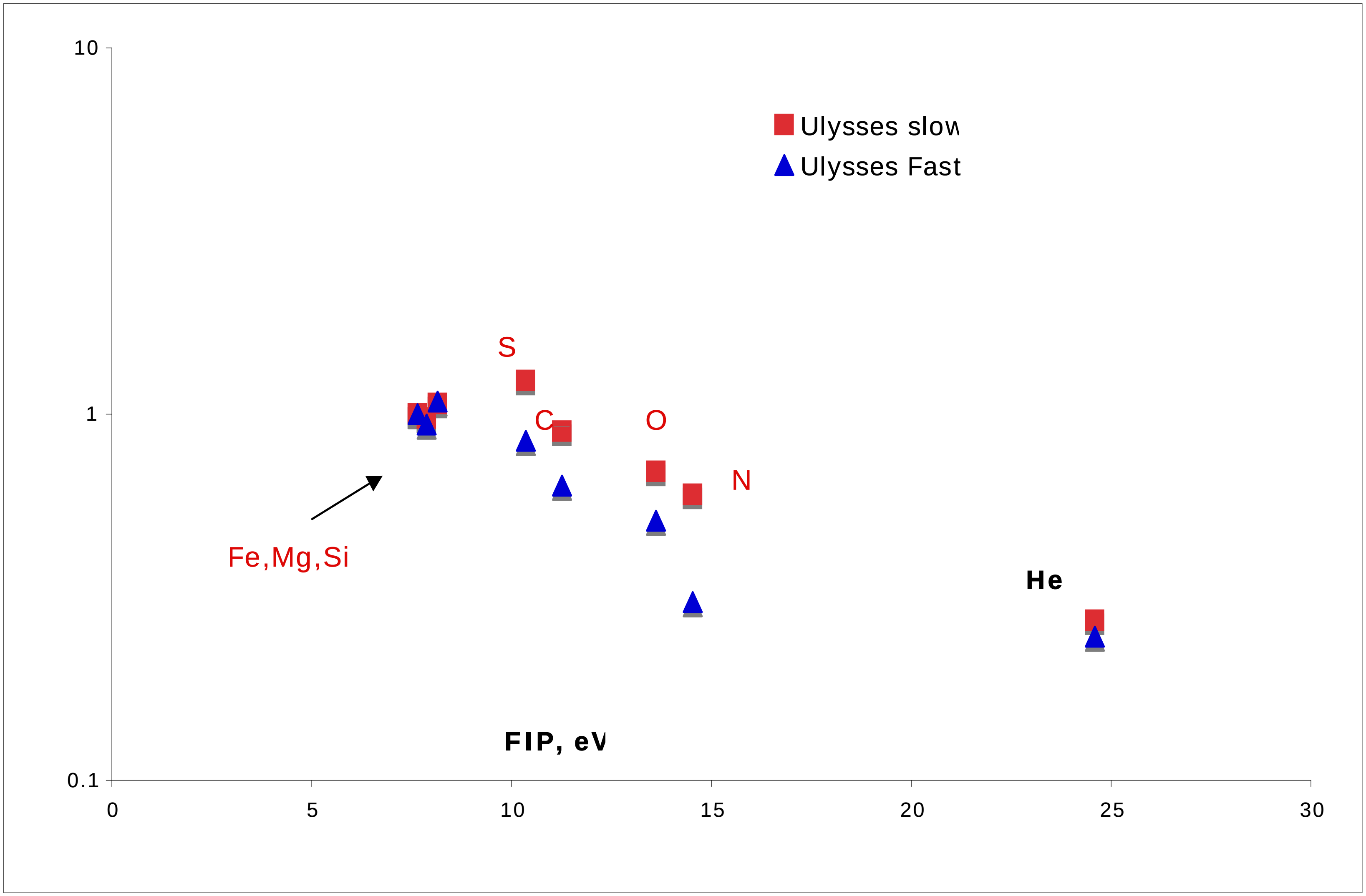
Slides 24-27 are background, unchanged from earlier GPMC.

- **Spacecraft data have shown that high first ionization potential (FIP) elements are depleted in solar wind compared to solar surface (photosphere).**
  - **e.g. Fe/He is higher in SW than in photosphere.**
- **Data for most easily-ionized elements (FIP < 9eV) appear unfractionated.**
  - **Most of elements in terrestrial planets have FIP<9eV**
- **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 i*sotope* ratios expected to be same.**

Fractionation Factor

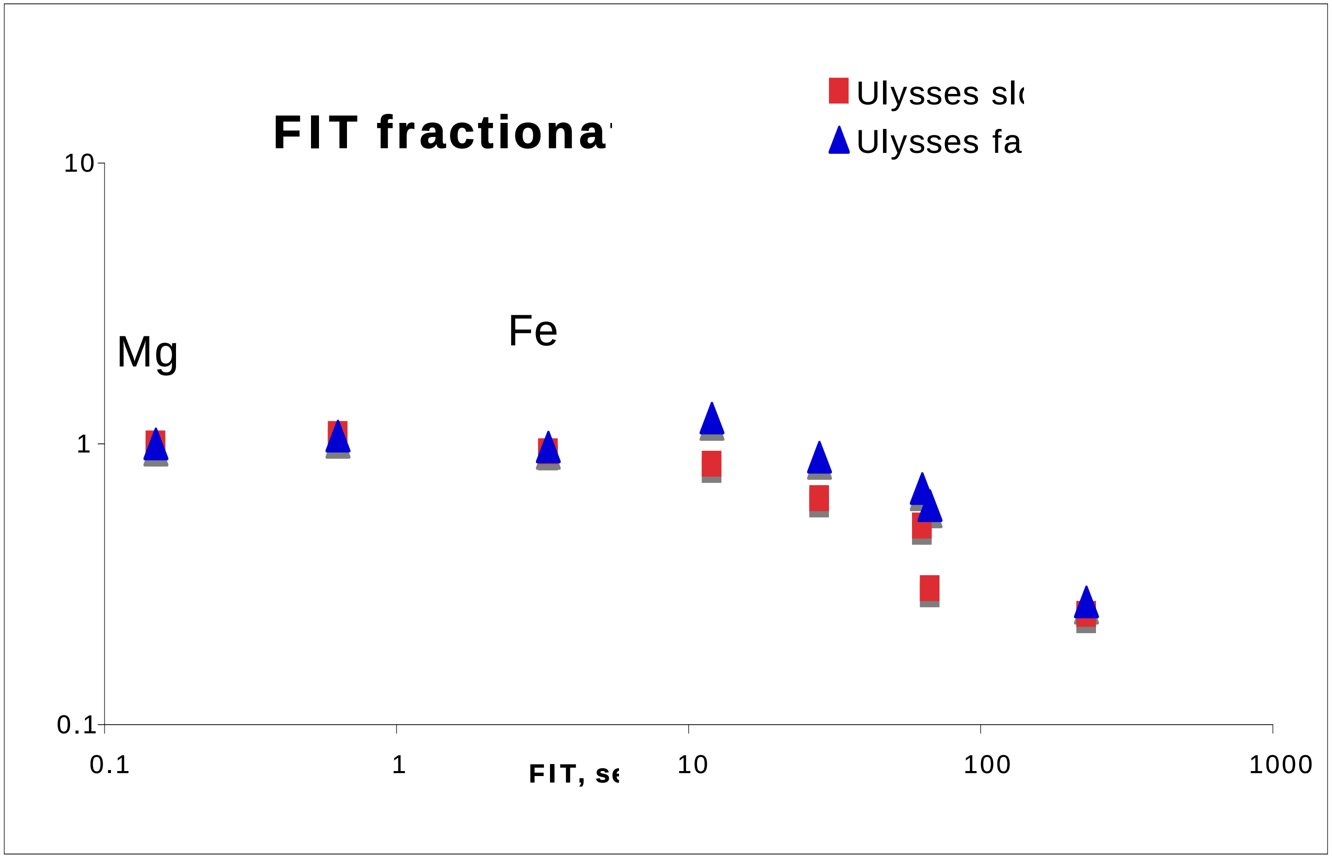
$$F = (X/Mg)_{SW} \,/\, (X/Mg)_{photosphere}$$

FIP Plot from spacecraft data



FIT (first ionization time) plot from spacecraft data

FIT is an estimate of the time required to ionize a neutral atom upon transport from the lower temperature photosphere into the solar corona, from where the ion will be accelerated and incorporated into the solar wind. FIT is more physical than FIP, but is model-dependent. Data plots using FIT are cleaner than those with FIP with the 9eV fractionation cutoff (translated to about 20 sec ionization time) showing clear depletions of high FIP/FIT elements.

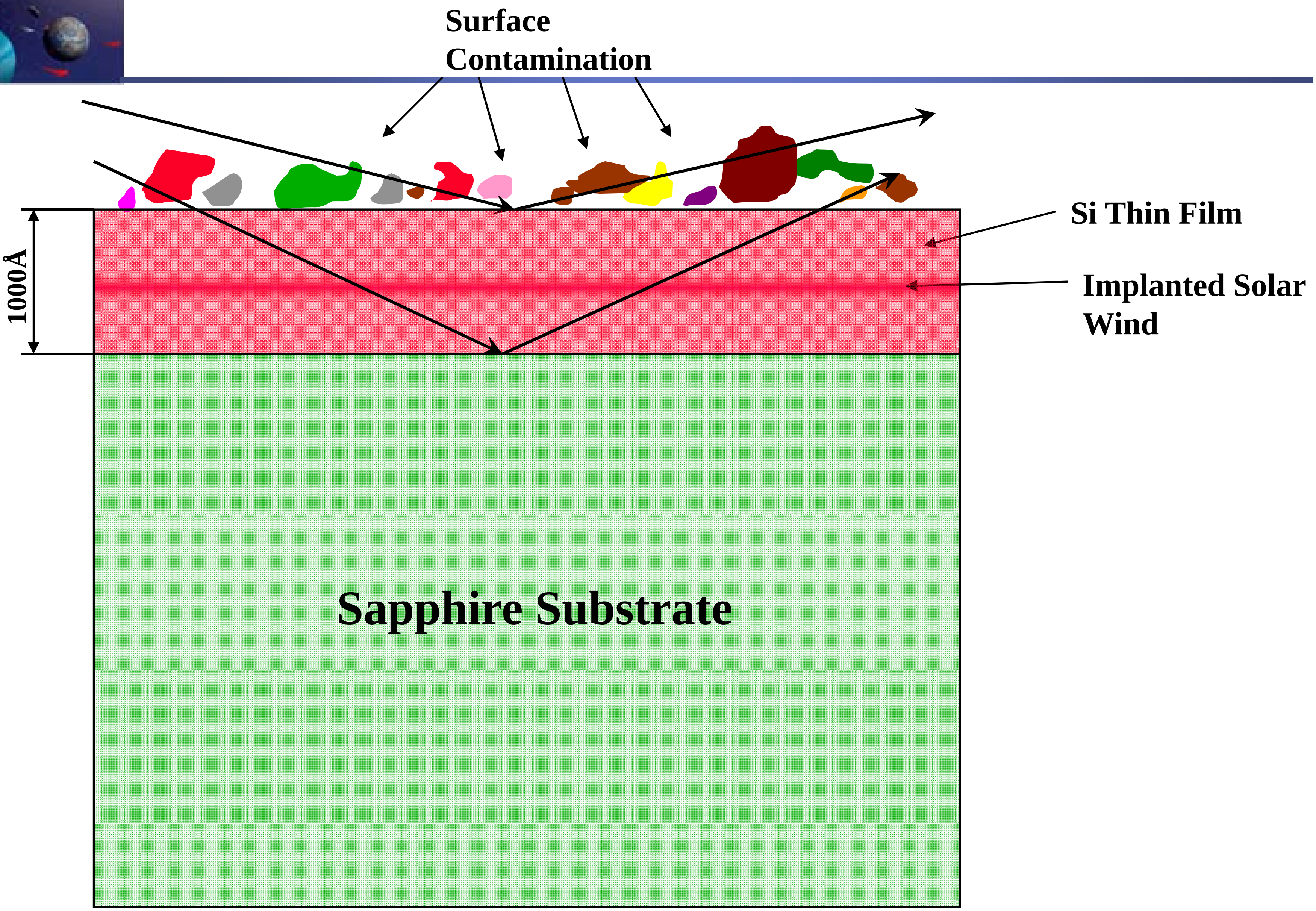


Fe/Mg analyses by SIMS (Jurewicz et al., ASU)

- 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 ^{25}Mg as internal standard into flight samples.
- Unlike Mg, good agreement for Fe fluence obtained between two materials.

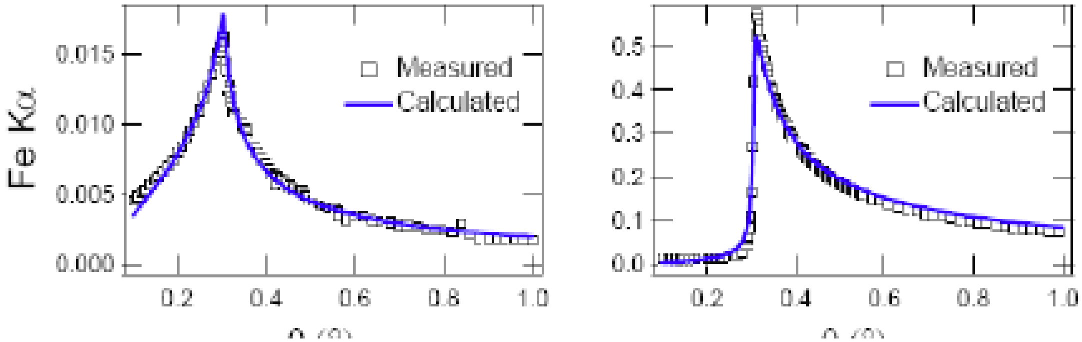
TRXRF Kitts et al; APS/ANL

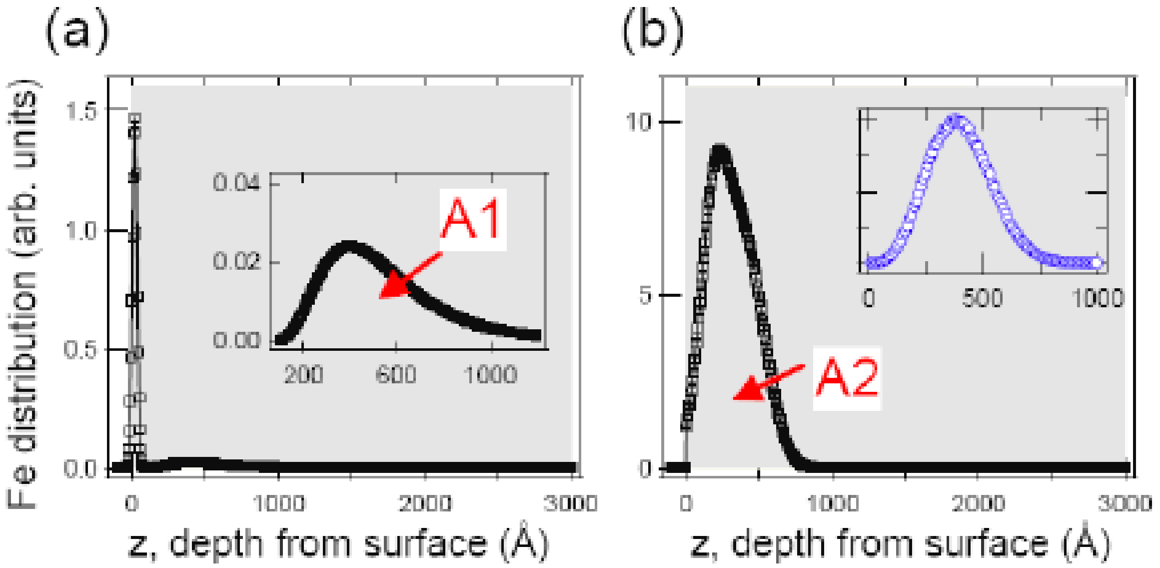
- Analytical Application of Snell’s Law.
- Intense collimated beam of monoenergetic synchrotron radiation photons incident at angles near the critical angle.
- While being reflected, photons induce fluorescent X-rays from elements in near surface regions (see following page).
- Small variations (0.x degrees) in tilt angle probe below surface to solar wind depths, resolving surface contamination from solar wind.
- Minimal penetration surpresses continuous X-ray background giving high signal/noise.
- Sapphire and SoS identified as optimum materials.
- Depth resolution allows separation of surface contamination, but cleaning still desirable; tests in progress.


Surface Contamination
Si Thin Film
Implanted Solar Wind
1000Å
Sapphire Substrate

Kitts et al LPSC (09) presentation

(a) flight sapphire 50722 **(b) Fe implant standard**





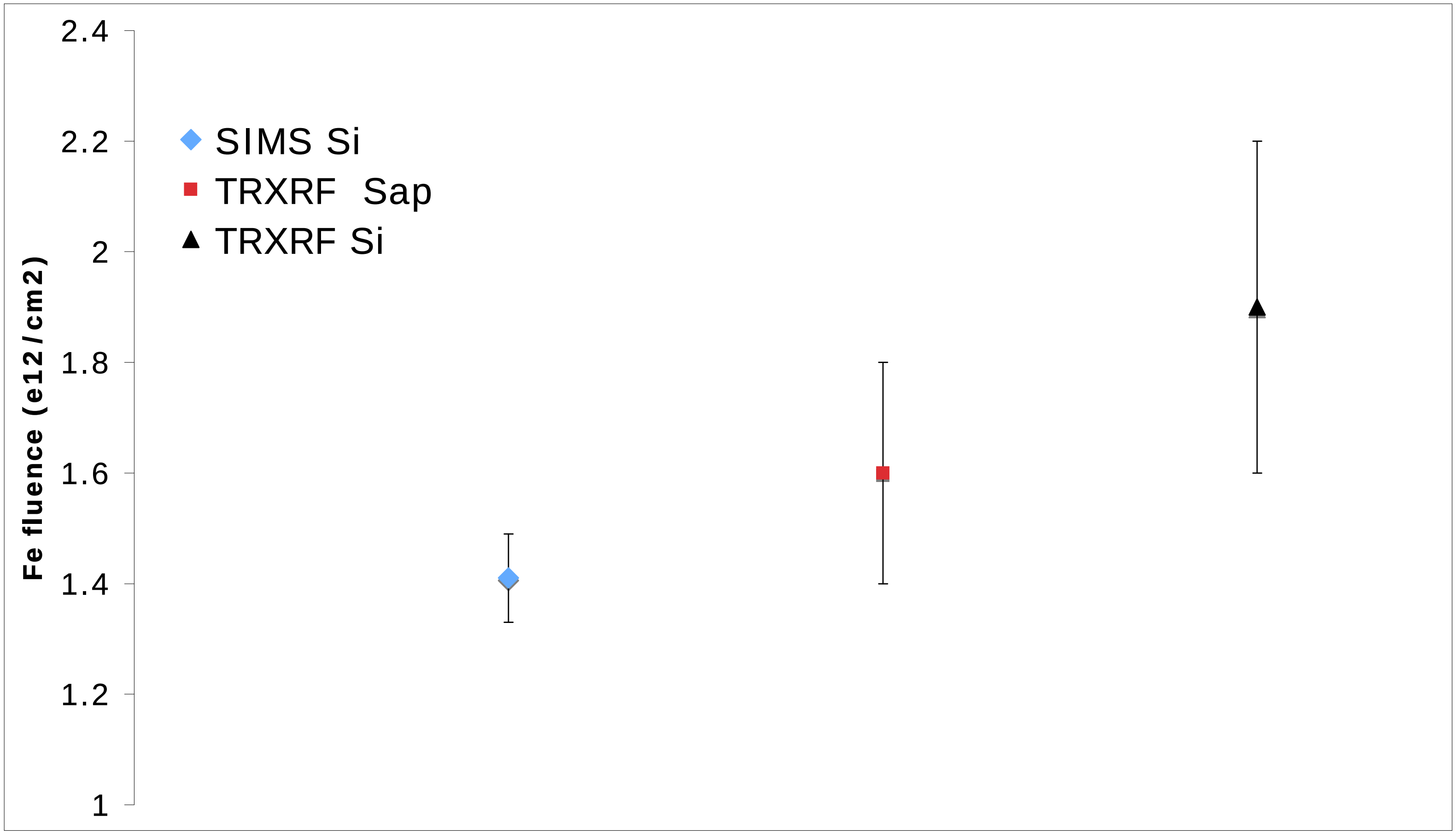
Upper curves are measured intensity of FeKα X-rays as function of tilt angle for flight sample and implant standard. Peak counting rate is observed at the critical angle.

The observed intensity below the critical angle on the flight sample is due to a much larger amount of surface contamination than on the implant.

Inversion of the FeKα profiles gives the depth distributions shown in the lower figures. The (a) inset shows the derived solar wind Fe distribution. The inset in (b) shows the theoretical (TRIM) implant distribution which agrees well with the TRXRF inversion.

Profiles can be measured at different incident photon energies as an additional check on the accuracy of derived solar wind fluences.

Fe fluences


2.4
2.2
2
1.8
1.6
1.4
1.2
1
Fe fluence (e12/cm2)
◆ SIMS Si
■ TRXRF Sap
▲ TRXRF Si

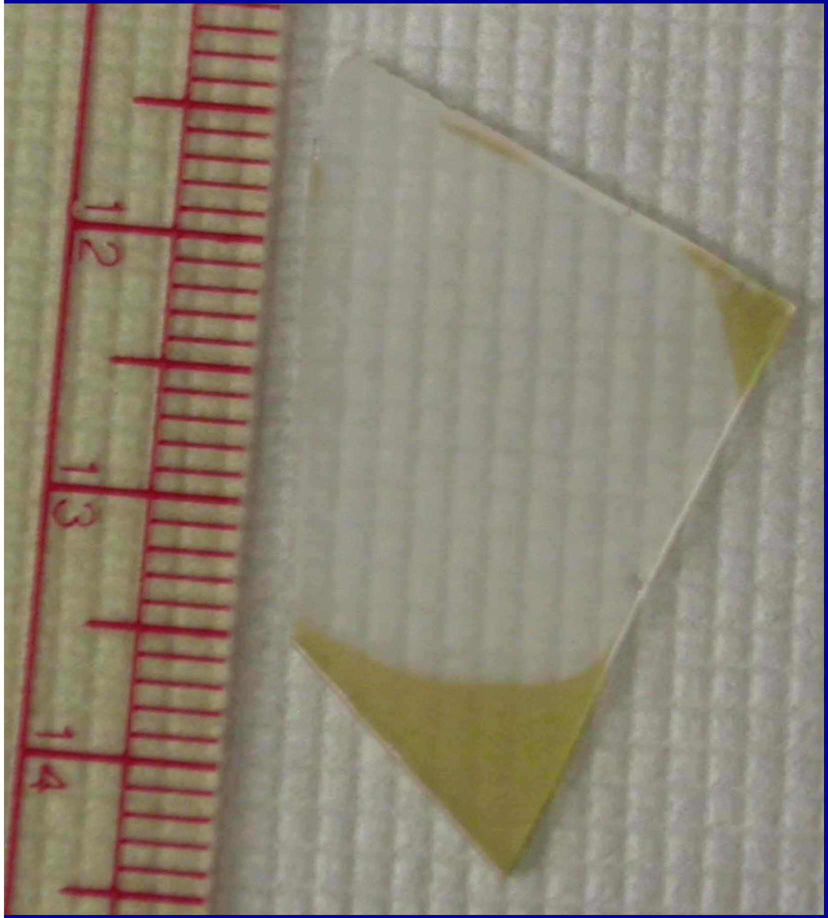
Fe fluences: Discussion

- The SIMS fluence on the preceding slide is based on July 2007 data from analyses done using optimum control of analytical conditions. The error bar only represents the precision of the analyses. Independent calibration of the Fe implant standard is underway and is discussed below.

- Independent TRXRF estimates of the Fe fluence from sapphire sample 50722 can be obtained by inverting the Al Kα angular response or by use of an Fe implant standard. The known stoichiometry of sapphire normalizes the solar wind fluence without reference to the data on the implant. Two different implants have been used with 5% agreement obtained. Both the implants and the Al normalization give an Fe fluence of $1.6 \pm 0.2 \times 10^{12}$ atoms/cm^2.

- The 60171 Si sample has a poor surface, and the fits to the angular profiles are not as good as those for the sapphire. However, the calculated Fe fluence agrees with that from sapphire at the one sigma level of the Si analysis.

ICPMS Mg fluence measurement: M. Humayun, FSU

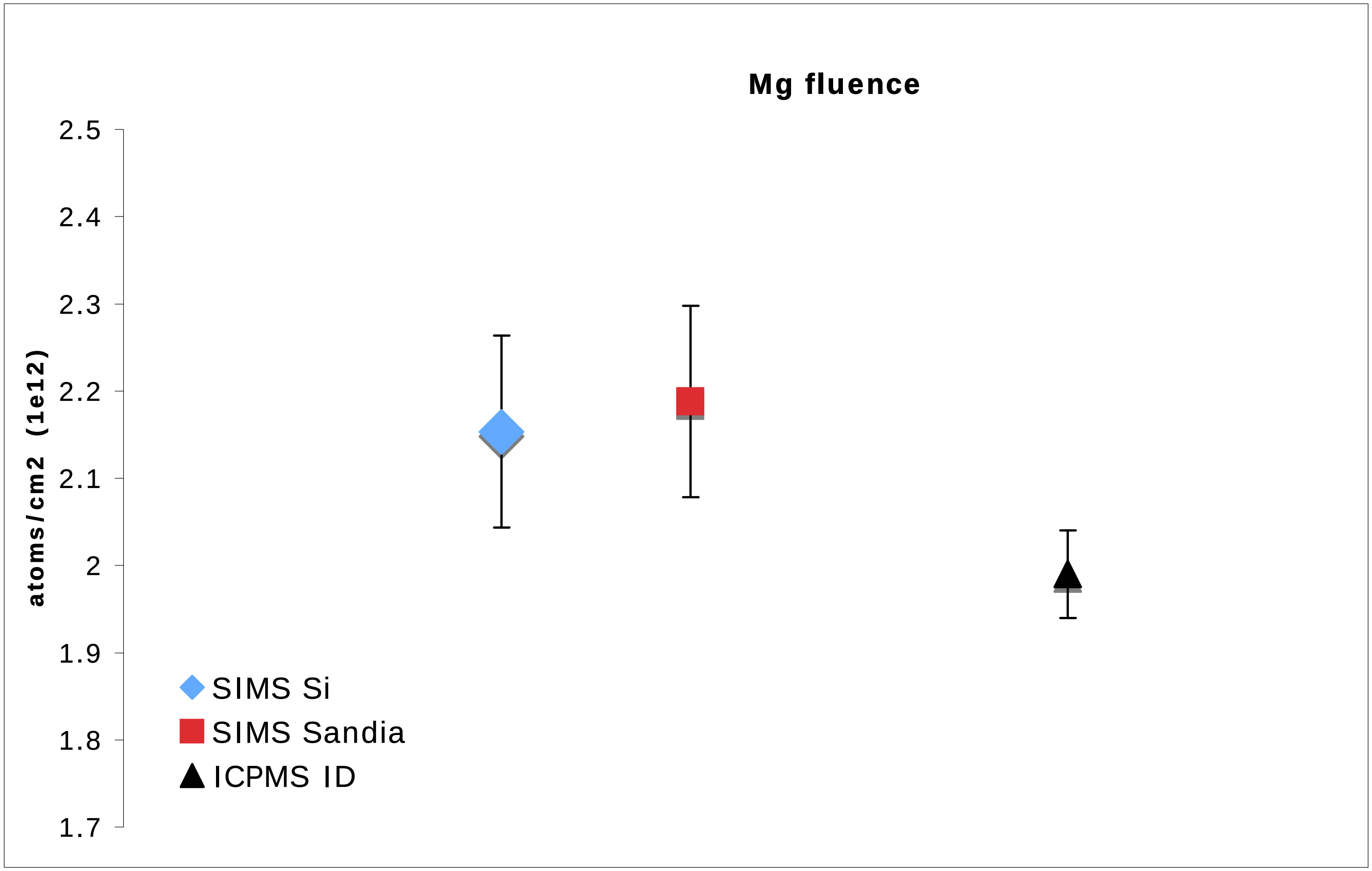


Flight SoS 50030

- Mg determined by isotope dilution;
- Si determined by external standardization.
- Sample cleaned with aqua regia until no Mg observed in leaches.
- Mg: 5.21 x 10^{12} ±1.2% (2σ) atoms
- Si: 2.08 x 10^{18} ±5% (2σ) atoms
- Area removed=2.47-2.76 cm^2, assuming a thickness of the Si layer of 170-190 nm, vs. geometrically measured area =2.76 cm^2.

Mg Fluence: 1.99 x 10^{12} ±5% (2σ) atoms/cm^2

Bulk solar wind Mg fluences

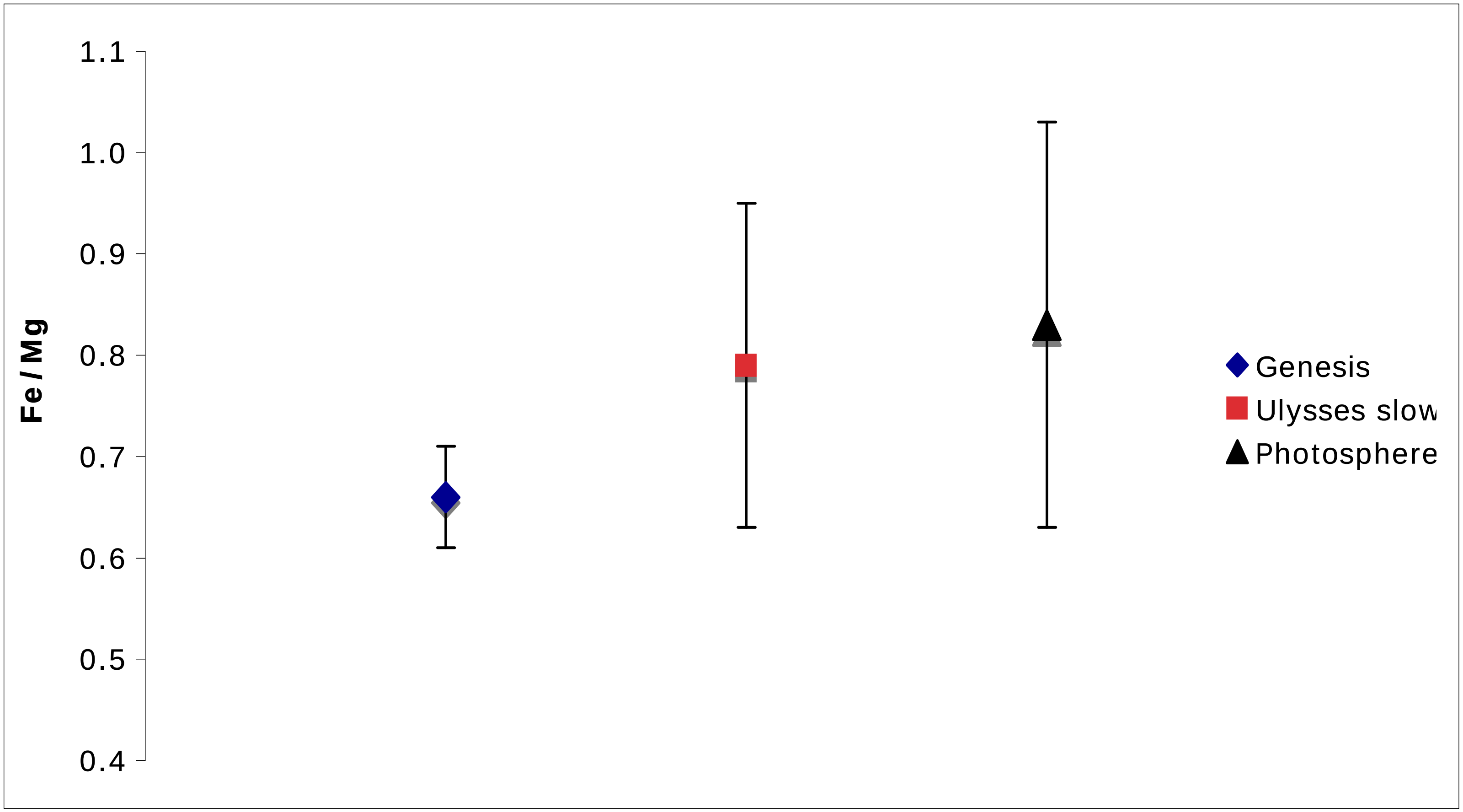


Mg Fluence: Discussion

- **For the ICPMS ID measurement, precision is accuracy.**
  - **The measured concentration will increase by a few % to allow for solar wind Mg implanted beneath the Si into sapphire.**
- **Error bars on SIMS fluences represent precision. Independent calibration of implant fluence standard in progress, discussed later.**

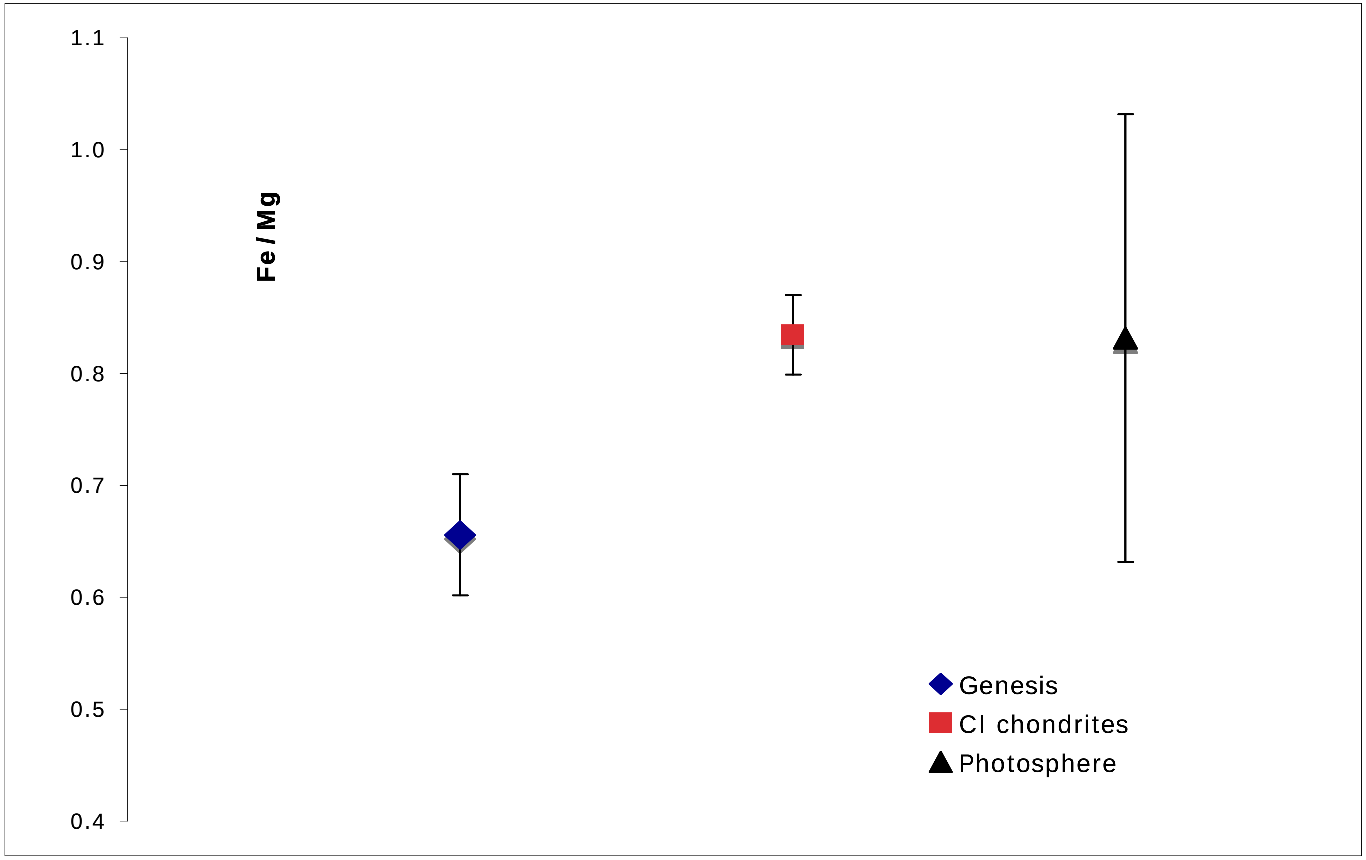
Comparison of SIMS data with photosphere and spacecraft Fe/Mg

(next two slides unchanged from Aug 2008 GPMC)



All data sets agree within errors of other data. No evidence for FIP (FIT) fractionations. Both Fe and Mg have FIP < 9 eV.

Compare Genesis SIMS with CI chondrites



Most compilations of "solar" elemental abundances based on CI chondritic meteorites. Justification for this is agreement with photospheric abundances. Genesis SIMS 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.

Calibration of Fe implant fluences

- SW fluence data on Sandia (diamond-like-C), SoS, and Si based on 4e13/cm^2 Kroko 2005 implant.
- Fluence can be independently analyzed on 5e15/cm2 Si implant by isotopic dilution on samples of known area. (ICPMS; FSU; in progress).
  - Measurement of high fluence implant in one material applies to all materials in same implant.
- Measurement of *relative* fluence measurement by SIMS of 5e15 and 4e13 Sandia implants is possible (ASU, CIW).
- High fluence implant also calibrated by RBS (ASU).
  - RBS data agree well (better than 5%) with fluence from ion implant integrated current.
  - RBS shows fluence uniformity to better than 1%.

Calibration of Mg implant fluences

- Three sets of 25Mg implants are available
  - HRL 2002, Kroko 2006, Kroko 2007 (K7).
  - SW data based on Si and Sandia using K7A internal standard implants into flight sample.
  - Control pieces of Si included in flight sample implants (K7A).
  - 2007 implant set has high fluence 25Mg implant (K7C) which can be analyzed accurately by isotopic dilution.
  - Independent calibrations by TIMS (JPL) and ICPMS (FSU) in progress.
  - *relative* K7C and K7A fluences for other implants can be measured precisely by SIMS
    - Replicate measurements at ASU and CIW have been carried out
    - Complications with dead time in high fluence samples, transient sputtering effects presumably under control.
    - Precision of profilometry pit depths has been an issue, but apparently resolved (following slides)

Precision of sputter pit depth measurements.

- **SIMS solar wind fluences based on concentration depth integral.**
- **Depth scale requires post-analysis measurement of depth of sputter pit.**
- **Discrepancy on some of the CIW K7C implant (previous page) pit depths:**
  - **Four different instruments have been used. Interferometers (UCLA, CIT) and stylus profilometers (ASU, NIST).**
  - **Two separate intercomparisons of ASU and UCLA on other samples have given good agreement.**
  - **A subset of the CIW K7C pits show a systematic 10% difference between the interferometer and stylus profilometer depths.**
  - **Two different instruments of each kind agree with each other, but the inter-instrument difference remains!**
  - **Nevertheless, when the K7C/K7A fluence *ratio* calculated using only interferometer or only stylus pits, good agreement is obtained.**
    - **saved by internal consistency !**

	K7A/K7C fluence ratio ($\times 10^{-4}$) CIW profiles
Stylus (NIST)	**3.51**
Interferometer (UCLA)	**3.47**

ASU-CIW comparison of K7A/K7C relative fluence

- Comparison on previous page involved only different depth scale calibrations for SIMS profiles of implants measured at CIW.
- Comparison of relative fluences from ASU and CIW:

	K7A/K7C relative ^{25}Mg fluence ($\times10^{-4}$)
CIW	3.49 ± 0.07
ASU	3.06 ± 0.21

It would be nice to have better agreement than this.

Part of the problem is trying to accurately measure fluences that differ by a factor of over 3000.

Plan: Isotopic dilution calibrations of K7C have no blank issues. Isotopic dilution measurement of K7A directly assumed to be difficult but if blanks good, may be possible to measure K7A directly. This will be assessed once isotopic dilution measurements of K7C are complete.

Calibration of K7C (3e15) implant with TIMS

Ngo, Papanasstassiou, JPL/CIT

Plan: Strip off implanted layer (0.5 μ for K7C) with HNO3/HF.

Obtaining uniform, controlled etching difficult, but

(HNO_3 / HF / H_2O) = (125 / 5 / 80) gives good result.

- **Followed etching rate by measuring weight loss on double-side polished FZ Si controls.**

K7C TIMS: Procedures are important

Approx 1 cm^2 K7C samples (Jurewicz)

areas measured accurately in A. Westphal lab (D. Woolum)

1. uvO3 cleaning at JSC to remove implant hydrocarbons.
2. Dilute (5%) HF to remove most SiO_2.

Steps 1 and 2 to make HNO_3/HF etching uniform.

3. HNO3/HF etching

   follow weight loss; few microns on average removed.
4. Repeat step 3 to check for complete extraction.
5. Spike etches and rinses with ^{26}Mg.

No implant ^{25}Mg measured in three separate, step 4 re-extracts.

Results

Nominal K7C fluence: 2.99 e15/cm^2

Sample	**^{25}Mg fluence(e15)**	**Percent Recovered**
K7C-5B	**2.1**	**69**
K7C-5C	**1.9**	**62**

5B - 5C fluence difference probably significant.

Interpretation

Replating ? $Si + Mg^{++} \rightarrow Mg + Si^{+4}$

Contradictory previous data on whether this happens. Not expected from EMFs (Munir)

Second re-extract of 5C with spike added to HNO_3 / HF; three times longer etch:

No measurable ^{25}Mg. No evidence for replating.

Contamination levels of Mg in Si very low, so replating issue can be decisively tested by total dissolution of K7C sample:

Sample K7C-5D: measured fluence/nominal = 0.618, in good agreement with result from etching.

Replating doesn't happen. Overall, good that it doesn't, but discrepancy remains.

?????? Hard to believe that fluence low by 40%

Fe looks OK from RBS.

Another Complication

HF etch of 5C: 0.03 e15 ^{25}Mg/cm^{2}.

Only 0.08% but shouldn’t happen.

- K7C implant is deep; could be more important for flight samples.
- Needs to be checked out.
- Shallow (1 keV/amu) ^{25}Mg implant available from Kroko 2005 implant. Very sensitive to any surface loss.

Cleaning up to Recover Science after Crash

Three necessary steps to recovery of science objectives:

1. **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 JSC GPMC contribution or 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 GPMC)

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-H_2O (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.**

Particulate contamination cleaning; pre 2008 summary

Micro90(commercial soap)(+- hot xylene): significant (x10/100 reduction)

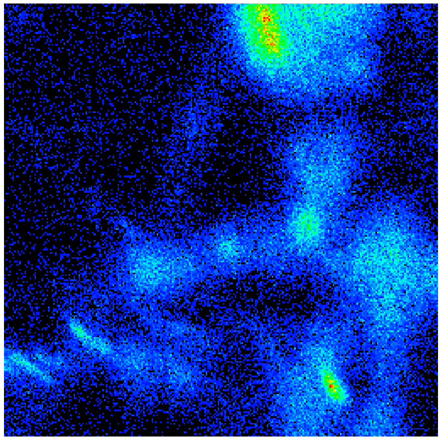
  - These 2005 studies for Mg(Si) complicated by lack of understanding of SIMS transient sputtering effects; confirmation required but acid cleaning seems preferable.

- HF: Concentrated acid can add residue particles (Westphal), but less apparent on controls (SIMS). Particle addition probably doesn’t happen with dilute HF, but no specific studies.
  - Dilute HF removes oxide layer from Si; unclear what happens to particles on top of oxide.
- HF/H_2O_2: Used to obtain sample for surface contamination analysis by semicondutor industry. Some older data suggest this adds residue particles on controls *and* flight samples (SIMS).
- H_2SO_4/H_2O_2 (Piranha). Used with some success on sapphire, but significant levels of Zn and Cr remain (Brennan, Pianetto SSRL)
- HF/HCl (“SC2”) good results in removing Na contamination on Si for SIMS analysis, although TRXRF analyses (May 07 GPMC report) showed significant quantities of many elements.

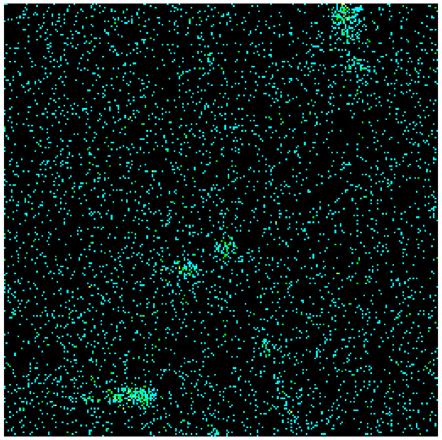
I. Lyon et al U. Manchester 60130 Si surface contamination by Time-of-flight SIMS (TOFSIMS)

- **Ozone + A2 acid (HF/HCl/H2O2) treated.**
- **No surface elements visible with XPS**
- **Was removed from shipping container and into cleaned prepared holder and into vacuum lock in <2 minutes**
- **Au$^+$ ions for high spatial resolution in ‘IDLE3’ instrument.**
- **TOFSIMS combines high spatial and mass resolution.**
  - **quantitation difficult**
  - **difficult to cover large areas**

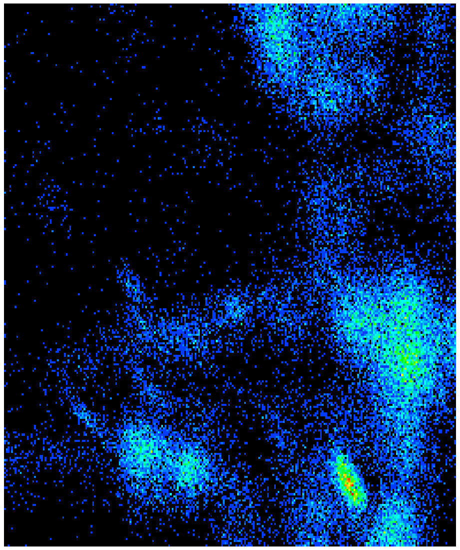
60130 TPFSIMS – Area 3 no presputtering



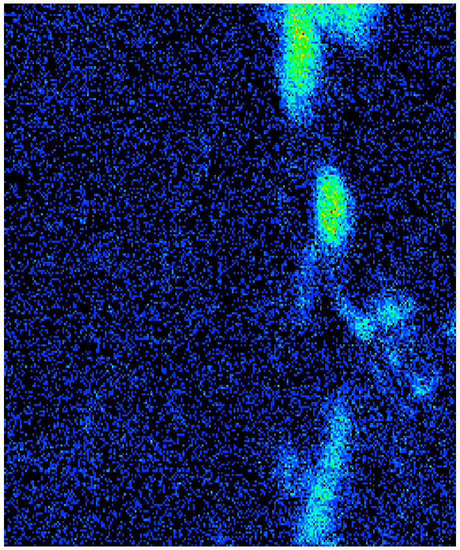
Na



Al



K



Ca

Field of view 100µm x 100µm

Two other areas analyzed qualitatively similar.

Being clean to XPS levels clearly not good enough.

Although difficult to quantify, the amounts of all elements are too high for large area analysis in this state of cleaning.

This area will be examined by SEM (Kuhlman) to identify the nature of the particles. Then cleaning procedures focused on removing these particles will be designed.

M. Humayun, FSU: ICPMS analyses.

Earlier sliide showed that Mg fluence in SoS sample 50030 gives good agreement with SIMS, but Fe fluence from same sample is about 40% higher than SIMS or SRTRXRF Fe fluence.

Successive steps of aqua regia cleaning of 50030 were carried out until insignificant amounts of Mg and Fe were observed. Then HF-HNO_3 dissolution removed Si from the underlying sapphire.

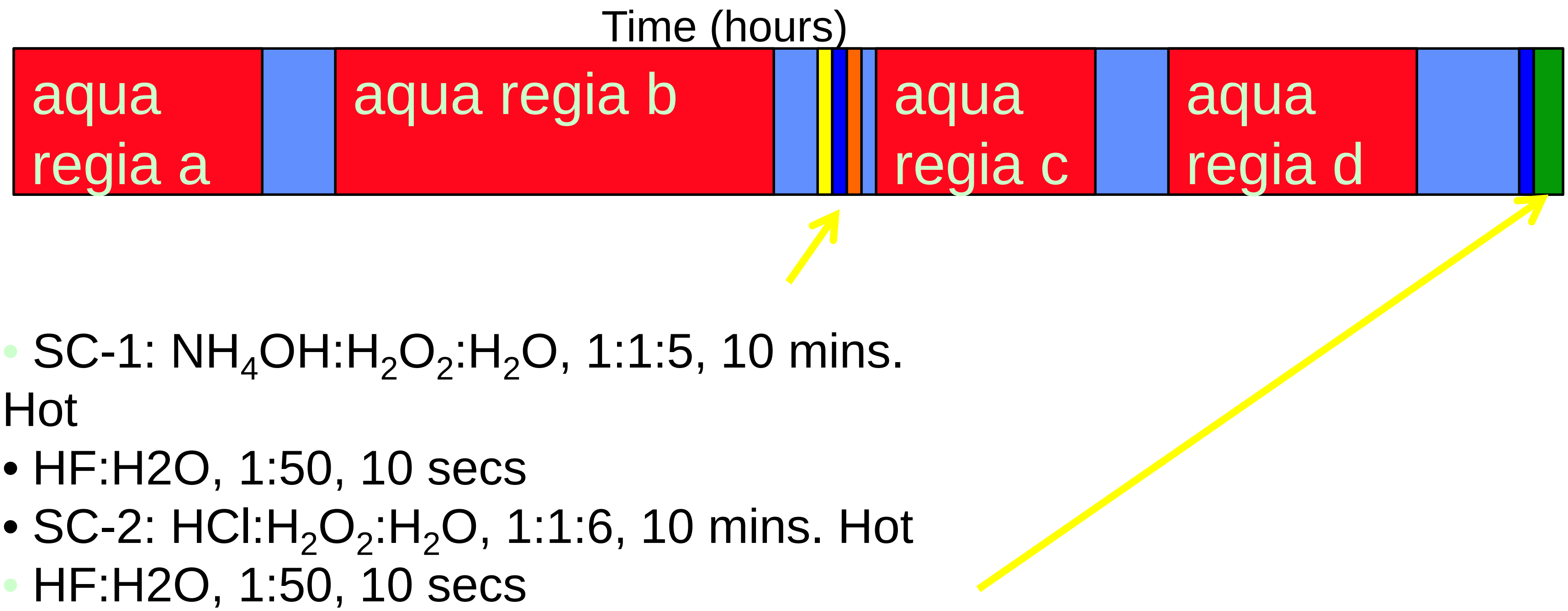
SIMS measurements indicate that the amount of Mg or Fe contamination on the Si-sapphire interface is small; however, the SIMS analyses refer only to areas of approximately 50 microns size.

A few small Fe-rich particles at the interface can never be ruled out.

Efforts started to analyze Si by differential etching of the Si surface with HF-HNO_3.

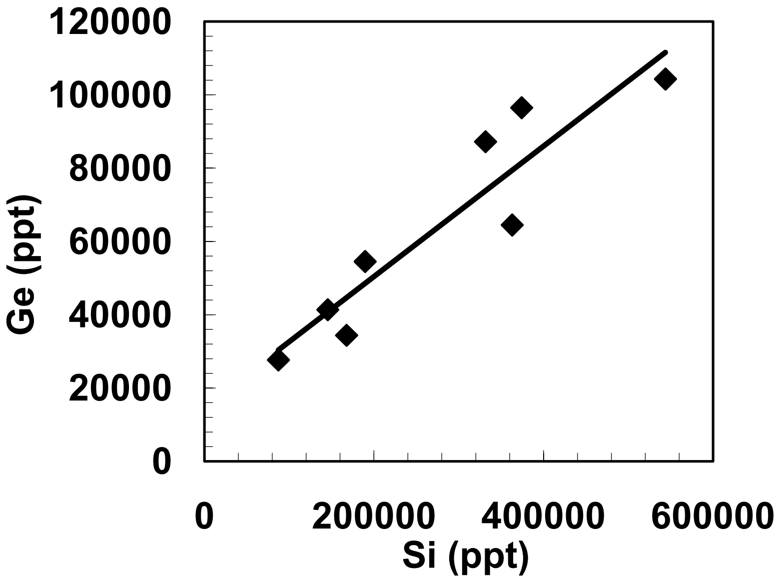
Humayun, FSU Acid cleaning: Si wafers

- Four steps of hot aqua regia attack (~88 hours total), with 1 hour ultrasonic cleaning between steps, produced a successively diminishing blank with Mg, Fe < SW values.
- RCA (SC-1 and SC-2) cleaning steps reduced many contaminants.



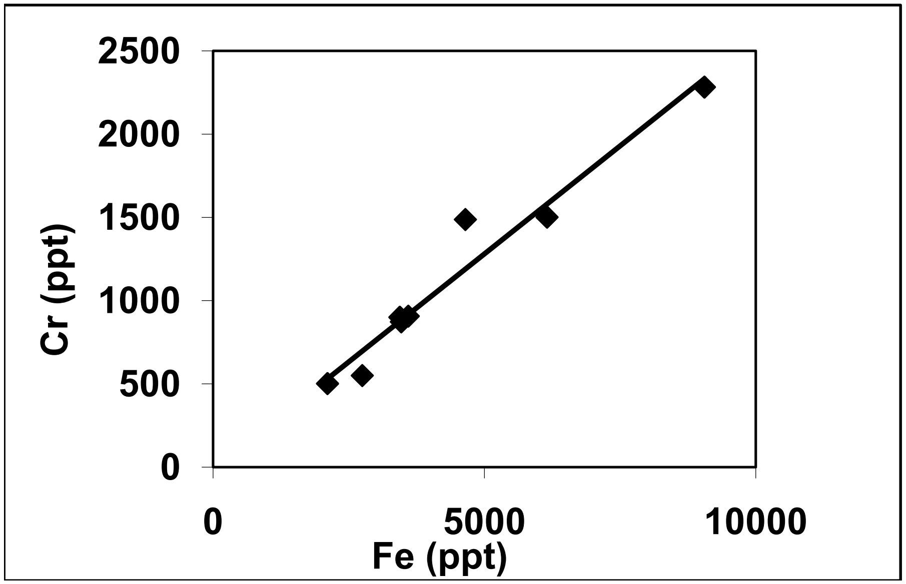
- SC-1: $NH_4OH:H_2O_2:H_2O$, 1:1:5, 10 mins. Hot
- HF:H2O, 1:50, 10 secs
- SC-2: $HCl:H_2O_2:H_2O$, 1:1:6, 10 mins. Hot
- HF:H2O, 1:50, 10 secs
- 4 steps: 10-15 secs of $HF:HNO_3:H_2O$ @ room T released 4, 5, 7, 8 µm-equivalents of Si

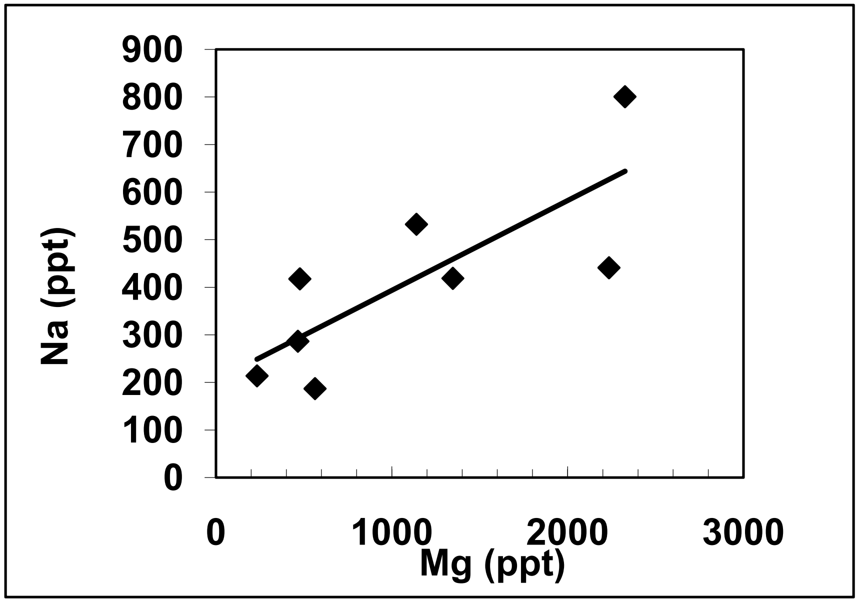
Chemical systematics: *first* aqua regia leach step of Si wafers



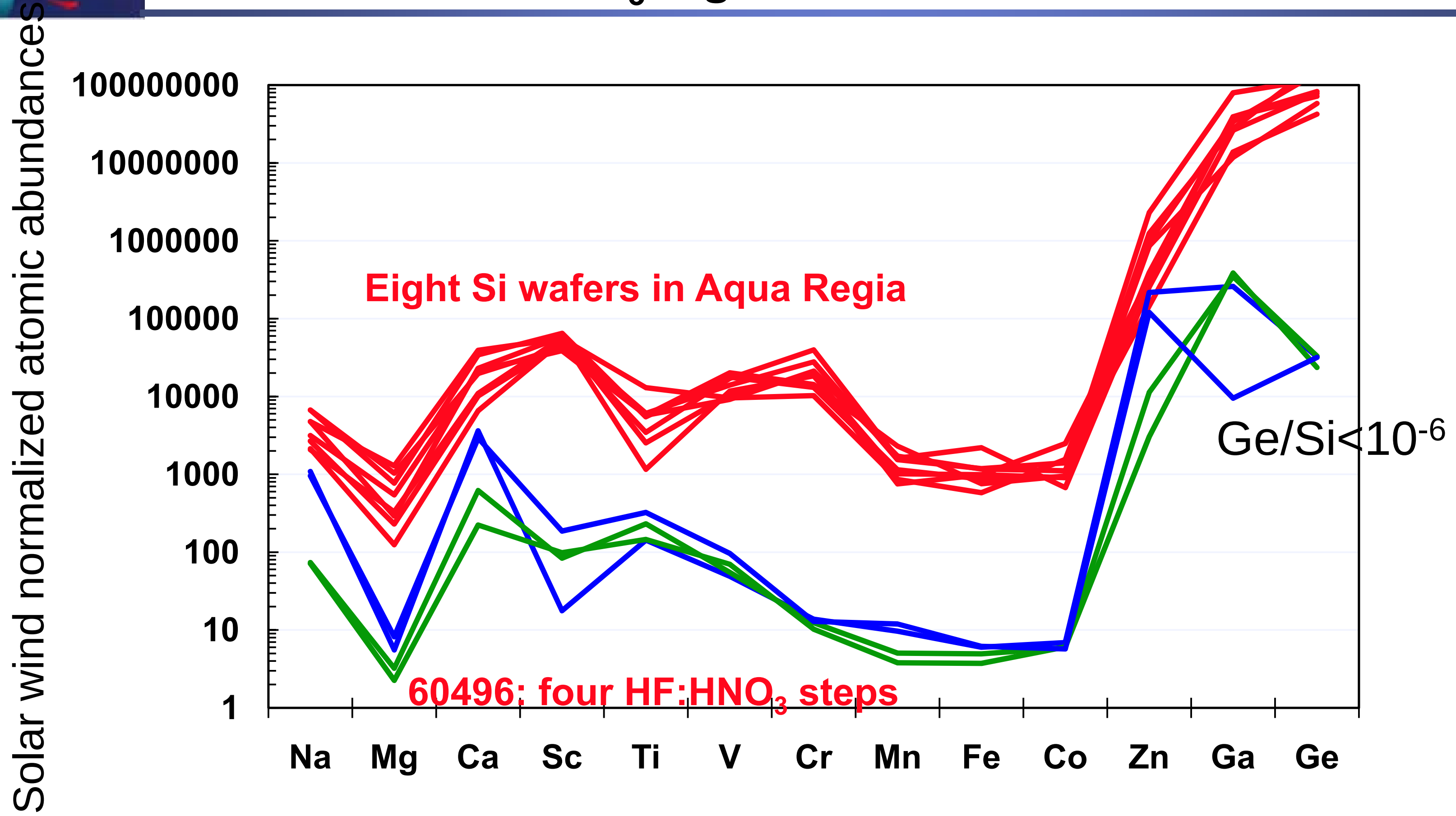
Eight 5-10 mm B/C array flight Si samples. Externally-standardized solution ICPMS. Concentrations refer to acid solution. The observed Si is probably from surface contamination and not from the Si wafer. The good correlation with Ge is surprising.

- **Ge/Si~ 0.2**
- **Fe/Cr~ 4 (stainless steel)**
- **Mg correlates with Na, Ca, and less with Ti, Si, and not with Fe. Mg, Ca, Na probably Utahogenic**





Comparison of chemical abundances in first AR step with final HF:HNO_3 digestions.

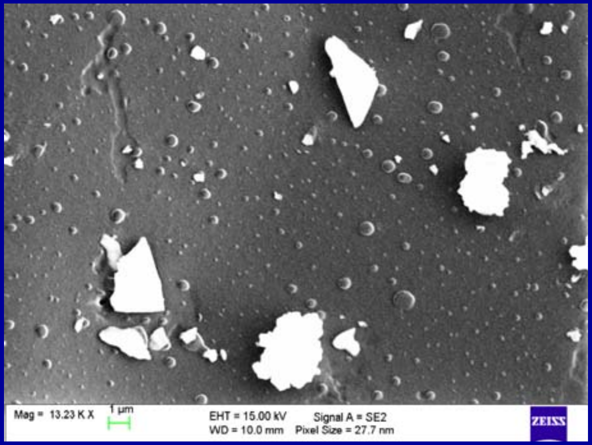


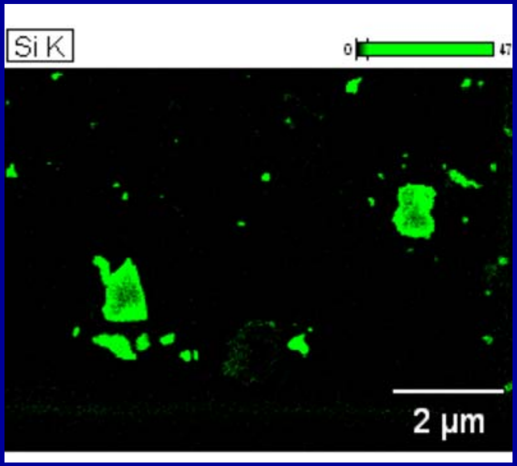
Acid cleaning never gets below SW levels for Si. Si very difficult to clean. Dirt in pits and scratches?

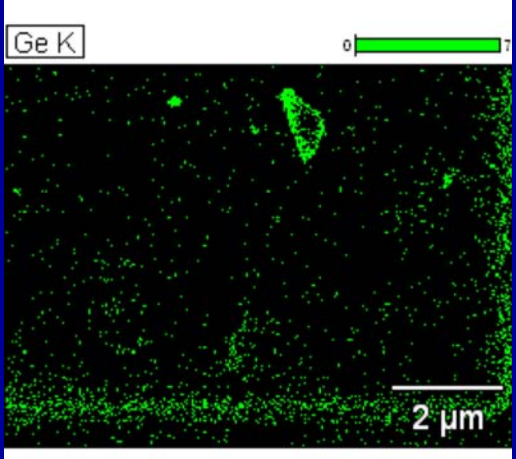
SEM studies of particles (Kuhlman, PSI, Wisconsin)

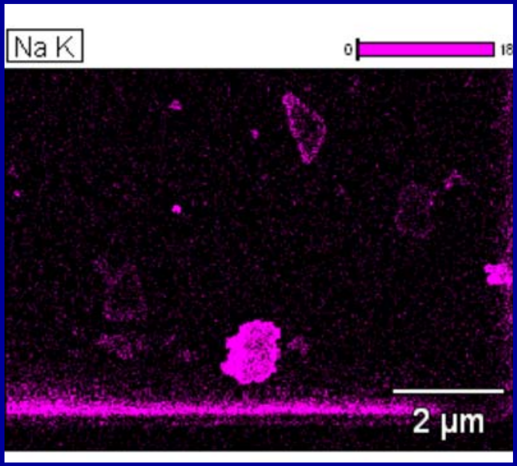
Sample 60121 – Uncleaned Si

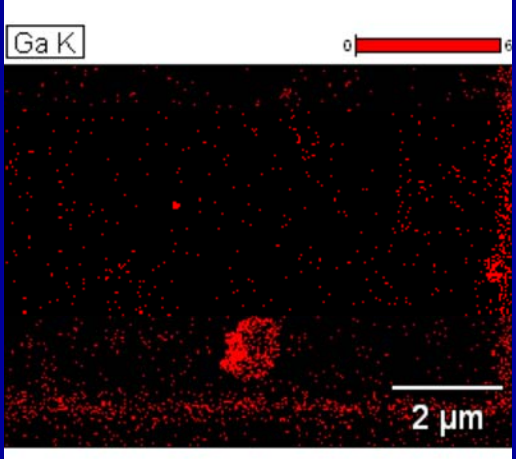
Particles removed with acetate film. Better SEM characteization than on Si surface.











SEM studies of acid cleaned flight Si (Kuhlman)

- Flight Si sample 60125 was particle cleaned with HF-HCl-H2O2 mixture A2 at Caltech.
- 67 of the remaining particles down to 0.3-0.5 micron identified by SEM by Kuhlman.
- No Utahogenic particles, stainless steel or Ge were found. These were probably originally present, and absence attributable to acid cleaning.
- Remaining particles were Si (probably collector array material), white paint crystals, and C (probably from SRC heat shield).
  - all previous studies indicate that micron-sized crash-derived Si particles on Si are difficult to remove. Some kind of impact welding has been suggested but this is speculation. Theoretically, this material is not a source of contamination, but Humayun results require this assumption to be re-examined.
  - White paint crystals are expected to be chemically resistant. They make large area analyses of Zn and Ga impossible, but effects on other elements unknown. It would be good to be able to remove them. Some success with acetate replicas.
  - C particles are a serious problem for large area analysis of C or N.
    - need to check on uv-ozone treated sample

Summary

Particle cleaning with A2 ($HF/HCl/H_2O_2$) acid mix (CalTech)

- A2 mixture of $HF/HCl/H_2O_2$; good results in removing inorganic contamination as mesured by XPS on SiC and CVD diamond and on control Si.

- Good particle cleaning by A2 on flight Si sample 650125 (Kuhlman; PSI; preceding page).

– XPS shows that A2 removes particulate (Na, S, Ca) contamination of flight DOS.

– Response of Si on flight DOS to A2 complicated. 2/6 samples appear to gain Si, but amount of loss for the other four large. (see previous report)

– Some suggestion that A2 removes brown stain directly, without ozone treatment. This requires confirmation.

– XPS measurable Ca contamination is removed from flight Si by A2, with no elements added, except Sn contamination from an unknown origin in two cases.

But, SRTRXRF on flight sapphire (Kitts, APS) showed significant contamination remained below XPS sensitivity levels.

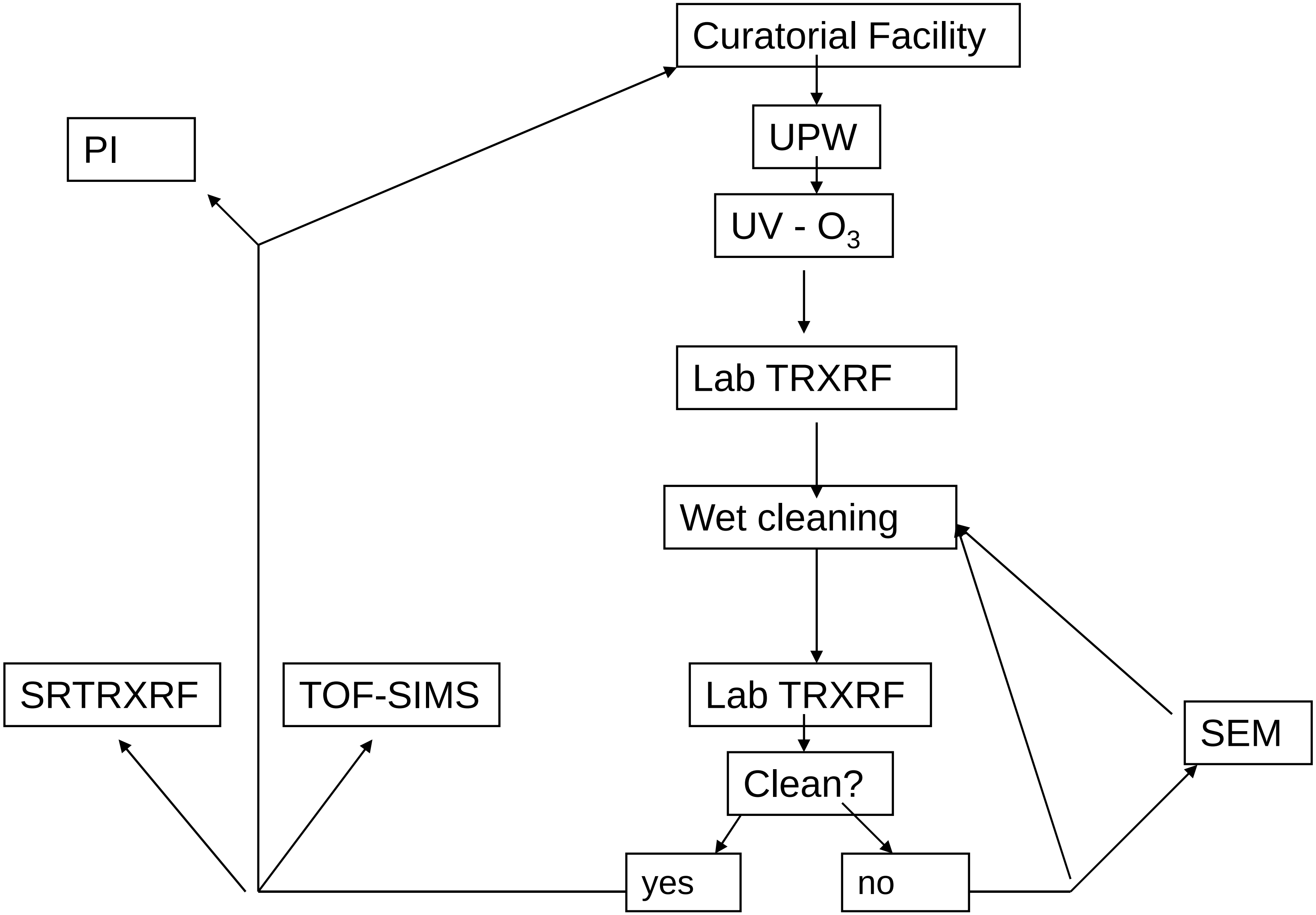
  – Unlike aqua regia, A2 does not roughen surfaces enough to interfere with SRTRXRF analyses.

A2 cleaned flight Si sample showed excessive Ca contamination during RIMS analysis (ANL)

A2 not good enough.

Need better contamination assessment than XPS

Master Plan for Sample Cleaning



Curatorial Facility

UPW

UV - O_3

Lab TRXRF

Wet cleaning

Lab TRXRF

Clean?

yes

no

SEM

PI

SRTRXRF

TOF-SIMS

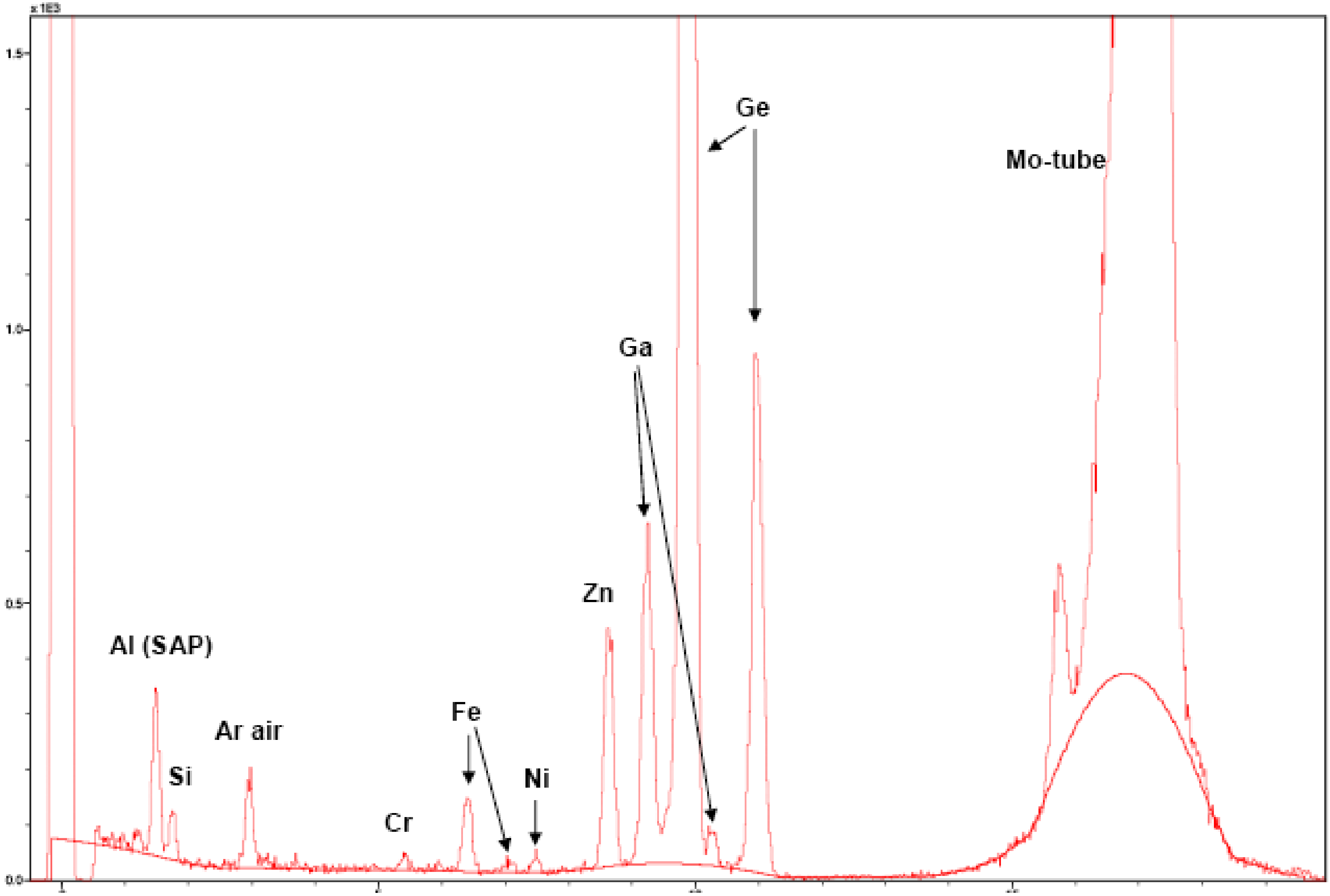
Master Cleaning Plan

- Discussion on pp 51-63 shows that we know a lot about particulate surface contamination.
- However, 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.
- Synchrotron radiation TRXRF (SRTRXRF) (APS) 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; otherwise technique is same as described earlier.
- XPS detection limits are ~ 10^{14} atoms/cm^2
- SRTRXRF has ~ 10^{10} atoms/cm^2 atoms/cm^2 detection limits.
- Lab TRXRF ~ 10^{11}- 10^{12} atoms/cm^2 detection limits achievable because of good signal/background and use of 10^4 - 10^5 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.
- Two laboratories identified with adequate capabilities: Loyola Chicago (M. Schmeilng) and NIU (L. Lurio). Sample spectra from Genesis flight sapphire in following slides.

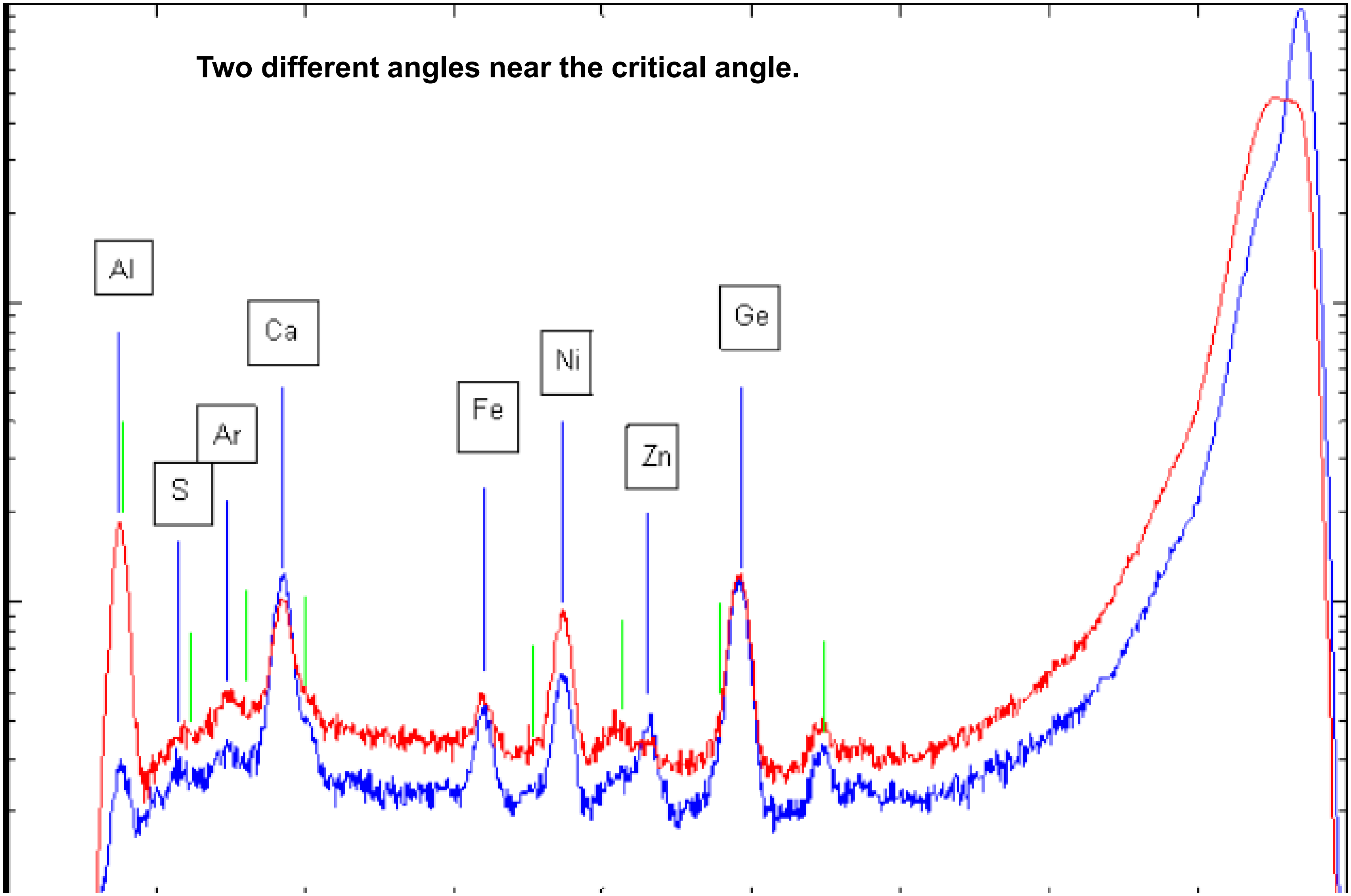
Loyola. UPW-washed sapphire 60679


Genesis Sample 60679, measured May 5, 2009 (10,000 seconds)

Spectrum slightly below critical angle to sample surface contamination

GENESIS

NIU UPW-rinsed sapphire 21022



Lab TRXRF, continued

- Spectra refer to mm-sized areas on cm-size flight sapphire samples. With samples of this size, analysis of several different spots possible.
- Single spot analyses on samples down to 7-8 mm size probably possible.
- As expected, amounts and nature of contaminants highly variable.
- Most peaks due to previously known contaminants:
  - Ge from collector materials powdered in crash.
  - Ga and Zn from SRC white paint.
  - Fe and Cr from stainless steel; powdered SRC material from crash.
  - Ca from Utah.
- Ni previously unrecognized.

Given the large number of analyses required, propose to send samples to both labs.

- Neither lab wants to spend full time measuring Genesis dirt.
- Estimated Genesis workload of about 60 samples/(lab-year).
  - LARS support proposals submitted.

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 10^{10} atom/cm^2 level.
- Pre-launch surfaces of some materials, e.g. sapphire, now known to be relatively dirty.
- Thus, assume that brown stain deposited on top of pre-launch surface contamination and must be removed. UV-ozone accomplishes this.
- SiO_2 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) will be involved in the wet cleaning phase. All three have access to clean labs and high purity reagents.

The general procedure will be for JSC-cleaned samples to be sent for Lab TRXRF. Analyzed locations will be recorded so that the same spot can be re-analyzed after wet cleaning.

Most collector materials are chemically inert, so cleaning trials to date have used acids, with recipes derived from the semiconductor literature.

There has been enough partial success with acid cleaning that this will be where our new efforts start. Exact recipes are under discussion.

Rather than going to flight samples immediately, we will start with flight spare controls. Here, it should be easier to produce lab TRXRF clean samples. This will also check that our packaging, shipping, and handling procedures are not adding significant inorganic surface contamination.

Limits of aqua regia cleaning in terms of TRXRF roughening will be determined.

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.

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.

The experience in SEM analyses of Genesis samples resides in Kim Kuhlman (PSI). She has developed acetate peel techniques that allow particles to be identified on insulating materials like sapphire and away from background X-ray interferences, e.g. Si particles on Si (see slide 59).

- Acetate peels will add organic contamination, possibly additional inorganic contaminants. These can probably be removed with hot xylene or some other organic solvent. XPS analyses, which are sensitive to the organic contamination, will guide the residue cleaning.

Many collectors are conducting, allowing particles to be measured directly on the samples.

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. These will be characterized on available paint coupons, starting with XPS.

If white paint removal becomes important, the acetate peel technique is the only approach we know of at present.

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. uvO_3 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 captial with the most sensitive SRTRXRF techniques (slides 23-25) or TOFSIMS (slides 53-54).

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

But we are a long way from this point.

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.

Specific Measurement Objectives (prioritized). Prelaunch.

(1) O isotopes.
(2) N isotopes in bulk solar wind.
(3) Noble gas elements and isotopes.
(4) Noble gas elements and isotopes; regimes.
(5) C isotopes.
(6) C isotopes in different solar wind regimes.
(7) Mg,Ca,Ti,Cr,Ba isotopes.
(8) Key First Ionization Potential Elements
(9) Mass 80-100 and 120-140 elemental abundance patterns.
(10) Survey of solar-terrestrial isotopic differences.
(11) Noble gas and N, elements and isotopes for higher energy solar particles.
(12) Li/Be/B elemental and isotopic abundances.
(13) Radioactive nuclei in the solar wind.
(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.
(19) Comparison of solar and chondritic elemental abundances.

Measurement of bulk solar wind except when noted.

Color-coded Science Assessment; updated 5/09

- 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.

Specific Measurement Objectives
(prioritized)

(1) O isotopes.

(2) N Isotopes in bulk solar wind.

(3) Noble gas Elements and Isotopes. (He, Ne, Ar Kr, Xe)
(4) Noble gas Elements and Isotopes; regimes (He Ne Ar, Kr, Xe).

(5) C Isotopes
(6) C Isotopes in different solar wind regimes.
(7) Mg,Ca,Ti,Cr,Ba Isotopes.
(8) Key FIP Elements (Na, Mg, Fe, Si, Ca, Cr, Ni, Al, C, N, etc)
(9) Mass 80-100 and 120-140 Elemental abundance patterns.
(10) Survey of solar-terrestrial Isotopic differences.
(11) Noble gas Elements and Isotopes: higher energy solar particles.
(12) Li/Be/B Elemental and Isotopic abundances.
(13) Radioactive nuclei in the solar wind.
(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.
(19) Comparison of solar and chondritic elemental abundances.

Summary (essentially 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 TRXRF and 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.