DUST-BUSTER—A new instrument of laser ionization of secondary neutrals time-of-flight mass spectrometer for isotopic analysis of pre-solar grains

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Relative abundance of the chemical elements in the solar system

Understanding the origin of the chemical elements: where and how?

General understandings:
Big Bang nucleosynthesis: P, D, He, Li, Be
Stellar nucleosynthesis:
Elements from C to Fe: fusion processes
Heavier than Fe:
- neutron rich elements: S-process--AGB
  R-process--SNe
- proton rich elements: Rp-process--accreting binary stars
  P-process—photo-disintegration-- SNe


Proofs of the theoretical predictions by astronomy observations

Evidence of nucleosynthesis in stars: Detection of Technetium absorption lines in certain red giants

Tc has no stable isotopes; longest half-life ~ Myrs;
$\Rightarrow$ Tc isotopes are synthesized fresh in the stars

Evidence of supernova nucleosynthesis: Detection of $^{56}$Co and $^{57}$Co gamma-ray lines from supernova 1987A.
Explosive Si-burning produces large amounts of $^{56}$Ni, $^{44}$Ti
$^{56}$Ni ($t_{1/2} \sim 6$ days) $\Rightarrow$ $^{56}$Co ($t_{1/2} \sim 77$ days) $\Rightarrow$ $^{56}$Fe
STAR DUSTS: Fossils of stars

3 μm SiC grain

5 μm graphite grain

TEM image of a 100nm thick slice of a 1 μm graphite grain
Dotted circle: TiC subgrains


Laboratory experiments to prove supernova nucleosynthesis

Figure 6. $^{30}$Si values plotted versus inferred $^{44}$Ti/$^{48}$Ti ratios for supernova SiC and graphite grains (Brommehn & Hoppe 2003, Hoppe et al. 2000, Nittler et al. 1996). The presence of extinct $^{44}$Ti in the grains proves a supernova origin.

NASA STARDUST comet sample return mission
Cometary dusts collected: Jan. 2, 2004
Earth returned: Jan., 2006

Description by artist about STARDUST spacecraft flying by comet Wild-2

http://stardust.jpl.nasa.gov

Aerogel collector, porous silica

Sample Return Capsule landed in Utah. Jan. 2006

View of a cometary impact into aerogel

X-ray Tomography Images of Wild-2 Comet Particles and Tracks in Aerogel (images by NASA/JPL)
Goal: look for large isotope effect in small grains

Cover as many as isotope ratios over large mass range in order to examine the structure of individual source star of solar system nuclides.

Technical challenge

Dust size < 1 μm
Weight ~10^{-12} gram
Atom numbers ~ 10^{10}
3σ ~ 10% effect

The new laser-SNMS instrument for Genesis by ANL
Ion optics simulation of the new instrument design

3D SIMION software was used to simulate, predict transmission and useful yield for the new reflectron time-of-flight (TOF) mass spectrometer.

Photoionization volume
4x4x3 mm³

Target
95% transmitted
to detector

97.22% before
Reflectron

95.29% after
Reflectron

Ion sputtering

Secondary particle

Laser-SNMS
Non-resonant
Single-photon
ionization

Resonant ionization

SIMS

mass analyzer

E & M

( Limited mass range )

RIMS

TOF

(Full mass range)

SPI

detector

Goal: instrument efficiency

\[
\text{Goal: instrument efficiency} = \frac{\text{# of ions detected}}{\text{# of atoms consumed}} \geq 30\%
\]
Ionization potentials of atomic elements vs. laser wavelength

- Free Electron Laser to 24 eV
- 157 nm (F₂ excimer)
- 193 nm (ArF excimer)
- 213 nm (Nd-YAG x5)

[Graph showing ionization potentials vs. atomic number Z with data points for Li, B, C, N, O, etc., and laser wavelengths.]
Assembled ion optics: front end photo-ion extraction system

Assembled ion optics: Photo-ion bending & detection housing

Assembled ion optics: Reflectron system; side & front views
US Air Force test pattern as viewed with our optical imaging system (Schwarzschild microscope)

Picture 1
TOF mass spectrum of the photoions from Ilmenite (FeTiO$_3$)

TOF mass spectrum of the photoions from Pyrite (FeS$_2$)
Data Analysis:

result: 100% x [(25Mg/24Mg)_{experiment}/ (25Mg/24Mg)_{terrestrial} - 1]

Correction: assumptions:

24MgH/24Mg = 25MgH/25Mg = 26MgH/26Mg = R

Intensity at mass 25 = 25Mg + 24MgH = m25
Intensity at mass 26 = 26Mg + 25MgH = m26
Intensity at mass 24 = 24Mg = m24

Abundance 24Mg:25Mg:26Mg = 78.99:10.00:11.01

Then, expected intensity

at mass 25 = (m25)_{expected} = (25Mg^+)_{expected} + R x (24Mg^+)_{expected}
at mass 26 = (m26)_{expected} = (26Mg^+)_{expected} + R x (25Mg^+)_{expected}
at mass 24 = (m24)_{expected} = (m24)_{measured}

R is found by minimizing

\[ [(m24)_{measured}-(m24)_{expected}]^2 + [(m25)_{measured}-(m25)_{expected}]^2 + [(m26)_{measured}-(m26)_{expected}]^2 \]

\[ (xMg^+)_{corr} = m(x)_{measured} - R x m((x-1)Mg^+)_{corr} \; ; \; x=25, 26 \]

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### Mg-Isotope Ratio

<table>
<thead>
<tr>
<th>Isotope ratio</th>
<th>w/o correction</th>
<th>with correction</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mg^+ (%)</td>
<td>MgO^+ (%)</td>
</tr>
<tr>
<td>25Mg/24Mg</td>
<td>11.7 ± 3.1</td>
<td>528.9 ± 8.6</td>
</tr>
<tr>
<td>26Mg/25Mg</td>
<td>2.1 ± 2.1</td>
<td>59.2 ± 7.4</td>
</tr>
</tbody>
</table>

### Ti-Isotope Ratio

<table>
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<th>with correction</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ti^+ (%)</td>
<td>TiO^+ (%)</td>
</tr>
<tr>
<td>47Ti/46Ti</td>
<td>4.0 ± 5.1</td>
<td>6.1 ± 3.2</td>
</tr>
<tr>
<td>48Ti/46Ti</td>
<td>0.7 ± 3.2</td>
<td>0.7 ± 1.3</td>
</tr>
<tr>
<td>49Ti/48Ti</td>
<td>27.9 ± 5.3</td>
<td>65.0 ± 4.1</td>
</tr>
<tr>
<td>50Ti/49Ti</td>
<td>12.4 ± 5.4</td>
<td>16.2 ± 2.4</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Isotope ratio</th>
<th>Cr^+ (%)</th>
<th>Isotope ratio</th>
<th>Fe^+ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>53Cr/52Cr</td>
<td>4.6 ± 5.6</td>
<td>56Fe/54Fe</td>
<td>1.5 ± 1.8</td>
</tr>
</tbody>
</table>
**S-Isotope Ratio**

<table>
<thead>
<tr>
<th>Isotope ratio</th>
<th>S⁺ (%)</th>
<th>S₂⁺ (%)</th>
<th>FeS⁺ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{34}$S/$^{32}$S</td>
<td>9.6 ± 3.8</td>
<td>-0.5 ± 1.0</td>
<td>3.8 ± 1.7</td>
</tr>
</tbody>
</table>

**Fe-Isotope Ratio**

<table>
<thead>
<tr>
<th>Isotope ratio</th>
<th>Fe⁺ (%)</th>
<th>FeS⁺ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{54}$Fe/$^{56}$Fe</td>
<td>3.3 ± 1.5</td>
<td>1.3 ± 0.9</td>
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</tbody>
</table>

**Conclusions:** the isotope ratios of the isotopes which have suffered less interferences from hydrides or hydroxides such as those of $^{48}$Ti/$^{46}$Ti, $^{54}$Fe/$^{56}$Fe in FeTiO₃ and $^{34}$S/$^{32}$S, $^{54}$Fe/$^{56}$Fe ...can be measured at a level that its deviation to the terrestrial ratio is within 1.5% at one sigma uncertainty level of better than 3%.

Things to be improved to make the DUST-BUSTER instrument ready for analyzing pre-solar grains:
1: up the instrument sensitivity ... >10%
2: implement a different type of ion gun—Ga⁺ gun for less than micron-sized beam spot size
**Technical challenge**

Small sample size
- ~ $10^{-12}$ gram
- <1 $\mu$m$^3$
- $10^{10}$ atoms

**Isotopic measurement techniques**

**TIMS:** thermal ionization mass spectrometry
- System sensitivity can be >$10^{-2}$, but ionization efficiency is element dependent

**ICP-MS:** inductively coupled plasma mass spectrometry
- System sensitivity ~ $10^{-3}$, element less dependent

**SIMS:** secondary ion mass spectrometry
- System sensitivity usually <$10^{-4}$, element dependent

**DUST-BUSTER**
- Laser ionization secondary neutral TOF mass spectrometry
- System sensitivity expected > 10%
Carbon and Nitrogen isotopic ratios of different populations of presolar SiC grains from Murchison carbonaceous meteorite.

S. Amari et al. APJ, Vol 559, P559, 2001