Trace, Isotopic Analysis

Michael J. Pellin, Michael R. Savina, and Wallis F. Calaway
Materials Science Division, Argonne National Laboratory
Emil Tripa, Yoav Kashiv, Andy Davis, and Robert N. Clayton
Enrico Fermi Institute, University of Chicago

Abstract

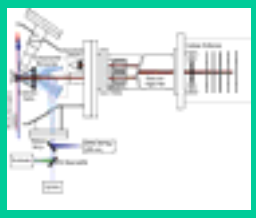
There exists an important class of analytical problems that require both sensitivity and discrimination. This class is exemplified by the increasingly stringent demands of the electronic industry for unambiguous quantitative identification of trace impurities in semiconductor materials at high lateral resolution. Recently, particulate analysis, the isotopic and elemental analysis of micron sized grains, has also began to occupy the analytical community. The difficulty in these two cases arises from the need to make the measurement before consuming the few atoms of the element of interest while discriminating against the vast excess of bulk atoms. Consider trace analysis of ppm Zr in a 1 micron sized SiC grain. This grain contains a little over 25000 Zr atoms, half of which are ^{90}Zr (the major isotope) and only ~700 are in the important (as we shall see later) ^{96}Zr isotope. Analysis is of course complicated by the need to discriminate bulk species, some of which (such as Si_3C) have nominally the same mass as the analyte.

Rational

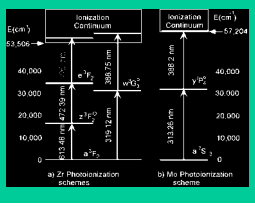
- **The isotopic content of a material may have a dramatic effect on a materials properties.**
  - Pure ^{12}C diamond has a significantly higher thermal diffusion coefficient.
  - Statistically nanometer sized objects will have a significant isotopic variation.
- **Isotopic Analysis is in many ways more challenging than trace analysis.**
  - System stability is strongly tested.
  - Sub "per mil" isotope ratios requires $>10^6$ counts in the *minor* isotope peak.
  - Every atom is needed if small samples are to be measured.
  - Minor isobaric interferences can skew results.
- **SARISA is ideal for such measurements.**
  - High Useful Yield.
  - Extreme noise immunity.
  - Absolute noise identification.
- **Initial Studies focus on meteoritic objects.**
  - Large anomalies.
    - Initial studies can achieve significant results.
    - Machine variations can be reduced while still producing important results!
    - Findings directly relate to how stars work – an important DOE mission.

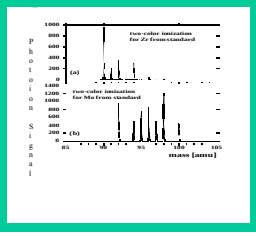
Method

Shown is a schematic diagram of the RIMS apparatus. There are two desorption sources shown – a DPSL Nd:YAG laser and an ion source (either a fine focused Ga^+ ion gun or a 5 keV Ar^+ source). When using laser desorption, the laser was brought onto the target through a Schwarzschild microscope that also allowed sample viewing using a dichroic mirror. Material atomized from the target was photoionized using any of several tunable dye lasers. The photoionized atoms are then pulse extracted into a time of flight (TOF) mass spectrometer whose reflectron was used to improve the mass resolution ($m/\Delta m > 1000$).



Isobars Eliminated!

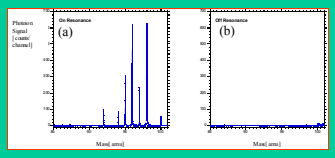




Mass spectra taken of the SRM 1264a (steel alloy) reference material which contains 0.49 % Mo and 0.069 % Zr (by weight). In spectrum a) 319.121 nm and 388.75 nm laser beams resonantly ionize Zr ($a^3F_2 \rightarrow w^3G^o_3 \rightarrow$ continuum), but not Mo as can be seen from the lack of signal at mass 98 for instance. In spectrum b) 313.26 nm and 388.2 nm laser beams were used to resonantly ionize Mo ($a^7S_3 \rightarrow y^7P^o_4 \rightarrow$ continuum), but not Zr as can be seen from the lack of signal at mass 90 for instance. In both cases, pulsed 355 nm laser radiation from a frequency-tripled Nd: YAG laser was used for sample ablation.

Background is determined!

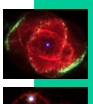
Photoion signal versus mass for (a) resonant laser tuned to the a^7S_3 ground state to the intermediate $y^7P^o_4$ state of Mo and (b) resonant laser detuned 0.1 nm. Note the lack of Zr and Ti_2 signal in either spectra.



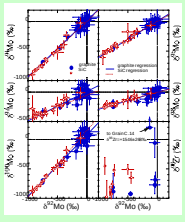
How Stars Produce the Elements

3 Types of element synthesis

- *s*-process
  - "slow" neutron capture
  - TP-AGB stars
  - solar type
  - "Cats Eye" Nebula
- *r*-process
  - "rapid" neutron capture
  - supernovae?
  - 1987A
  - neutron rich isotopes
- *p*-process
  - "photo-disintegration"
  - ????

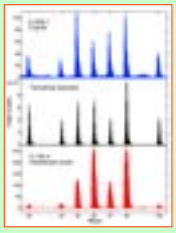


Mo Isotopic Studies
(SiC and Graphite) – mainstream grains

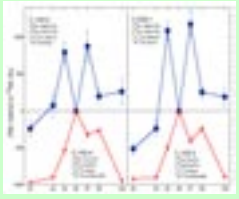


- *Only measurement of Mo in grains*
- s-process Mo; probably formed around low-mass (<5 solar mass) thermally pulsing asymptotic giant branch (TP-AGB) stars
- mixing line stretches from solar to pure *s*-process
- y-intercepts represent fraction of terrestrial ^{x}Mo which is *s*-process

SEM picture of 2 SiC grains culled from acid residues of the Murchison Meteorite (~2μm) in diameter. The one on the left condensed from an TP-AGB star. The one on the right from a supernovae.



- X-grain heavy elements are isotopically distinct from either terrestrial or mainstream.
- Presence of ^{96}Mo indicates significant *s*-process material present.
- All *r*-process isotopes show significant enhancements.
- $[Mo]_{X\text{-}grain} << [Mo]_{Mainstream}$
- ^{95}Mo and ^{97}Mo enhancements predicted by Clayton et. al.
- *p*-process isotopes, ^{92}Mo and ^{94}Mo, present but relative abundance's are different from terrestrial.



Recent results:

- Only heavy element (>Ti) measurements on single grains
- First definitive evidence for
  - –Mainstream *s*-process origin
  - –*r*-process X-grain origin
- A new type of nucleosynthesis
  - –Cross-section dependent
  - –Lifetime independent
- Ba
- A,B type grains

Publications:

Quantitative Elemental Analysis Using Laser Postionization Secondary Neutral Mass Spectrometry, Book Chapter in ToFSIMS: Surface Analysis by Mass Spectrometry, J. Vickerman, ed., Publisher Surface Spectra Ltd. and IM Publications (2001).

Barium Isotopes in Single Presolar Grains, Lunar and Planetary Science, Volume XXXII, pp. 2125-2126 (2001).

Toward Complete Isotopic Analysis of Individual Presolar Silicon Carbide Grains:C,N,Si,Sr,Zr,Mo,and Ba in Single Grains of Type X, Lunar and Planetary Science XXXI , (2000) 1934.

Zr and Mo Isotopic Constraints on the Origins of Unusual Types of Presolar SiC Grains, Lunar and Planetary Science XXXI , (2000) 1917.

Molybdenum isotopic composition of individual presolar silicon carbide grains from the Murchison meteorite, Geochim. Cosmochim. Acta, 62 (1998) 1097.

Strontium Isotopic Composition in Individual Circumstellar Silicon Carbide Grains: A Record of s-Process Nucleosynthesis, Phys. Rev. Lett. 81(1998) 3583.

Zirconium and Molybdenum in Individual Circumstellar graphite grains: newisotopic data on the nucleosynthesis of heavy elements, Astrophys. J. 504 (1998)492.

s-Process zirconium in presolar silicon carbide grains, Science, 277 (1997) 5330.

Basic Energy Sciences
Argonne National Laboratory
Materials Science Division
Surface Chemistry
FWP 58600