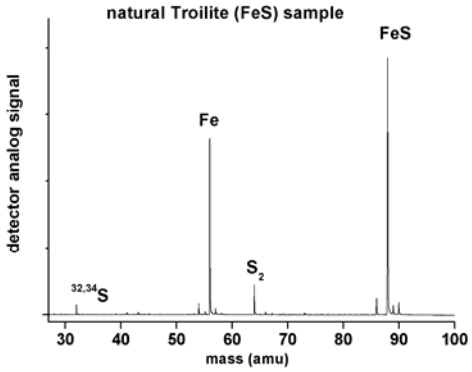
Developing SNMS for full-spectrum high-sensitivity in-situ isotopic analysis of individual comet grains collected by Stardust †. Chun-Yen Chen[1], Jason Jiun-San Shen[1], Typhoon Lee[1], Wallis Calaway[2], Igor Veryovkin[2], Jerry Moore[2] and Michael Pellin[2],[1]Insitute of Earth Science, Academia Sinica, Taipei, Taiwan, R.O.C.; [2]Materials Science Division, Argonne National Laboratory, Argonne, IL, U.S.A.

Introduction: In anticipation of the return of comet (and ISM?) dust grains by the Stardust mission [1] in mid-January next year, Academia Sinica (AS) and Argonne National Laboratory (ANL) have entered into a collaboration to develop instrument and method for the isotopic analysis of these samples. We need to achieve the highest possible sensitivity so that we can analyze individual grains one at a time to the smallest possible size. Only by doing so can we hope to reach one of the main science goals of the mission, namely the recognition of those isotopically distinct grains each carrying the characteristic signature of a particular nucleosynthetic stage of its parent star. In order to facilitate the interpretation of these grains the second requirement of our method is that the measurements must be made over the widest possible mass range before samples exhaustion. For instance, the thermonuclear fusion reactions that produced the isotopes of various major elements of a wide mass range required drastically different temperatures. Therefore their abundances could constrain the conditions at greatly varying depth inside the source star hence its structure and evolution.

For high sensitivity, we decided to select Secondary Neutral Mass Spectrometry (SNMS) with post-ionization by VUV laser because in the secondary particles released from the sample surface bombarded by primary micro-beam of ions or photons, the neutrals outnumber the ions by a factor of 100-1000. Using a new design of the extraction optics, the ANL team has been able to demonstrate experimentally that the useful yield (i.e. ion detected over atoms consumed) of their improved SNMS with post-ionization over a large volume (3x3x4 mm^3) using 157 nm VUV photons from an F_2 excimer laser is at least 12%. The entire mass spectrum is obtained by using a 3 m long reflectron type of time of flight (TOF) analyzer. One (SPIRIT) of the three such SNMS recently built at ANL is being used to explore analytical procedures for isotopic ratio measurements with non-resonant single photon ionization of multiple elements in complicated geological matrix. A new SNMS nicknamed Dust-Buster based on ANL design is under construction in Taipei.

So far we have measured 7 elements with 24 isotopes ranging from ^{24}Mg to ^{64}Ni. Sub-mm sample grains from six types of minerals were mounted on discs and polished for EPMA analysis in AS before SNMS at ANL using SPIRIT with MCP detector in the analogue mode. Non-resonant laser ionization lacks selectivity thus is vulnerable to interference which must be carefully evaluated case by case. However it can also ionize several different species containing the same elements thus allowing the measurement of the same isotopic ratios in different mass regions. Therefore, the same isotopic deviation if observed for several such species in the same sample would be much more trust worthy. An example of our multi-element wide mass range (30-100 amu) spectrum for natural troilites is shown in the Figure.



Sulfur was measured in three phases: S, S_2, and FeS while Fe was measured in two, elemental Fe and FeS. Note that our 157 nm (= 8 eV) VUV photons are not energetic enough to ionize elemental sulfur (ionization potential = 10 eV) in the single photon mode. We suspect the same for the sulfur dimmer S_2. Therefore it is not surprising both species showed low intensity resulting in rather poor reproducibility

of 5% (1 sigma) in the 34/32 ratios whose value is also too high by 15% probably caused by low level interferences. On the other hand the high intensity FeS mass peaks yield a much better 34/32 ratio within 1% of the normal with a 1 sigma precision of only 0.7 %.

Element	Isotope	Ion	Sample
Mg	24, 25, 26	Mg^+	Ruby Spinel ($MgAl_2O_4$)
			Synthetic MgO
			Rutile (TiO_2)
			Diopside ($MgCaSi_2O_6$)
Si	28, 29, 30	Si	Sphene ($CaTiSiO_5$)
S	32, 34	S^+, S_2^+, FeS^+	Troilite (FeS)
Ca	40, 42	Ca^+	Sphene
Ti	46, 47, 48, 49, 50	Ti^+, TiO^+	Sphene
			Rutile
Fe	54, 56, 57	Fe^+, FeS^+	Troilite
		Fe^+, $FeOH^+$	Iron meteorite
Ni	58, 60, 61, 62, 64	Ni^+	Iron meteorite

From the table above we can summarize the conclusions of our wide mass range multi-element LI-SNMS isotopic analyses as follows:

1. The ability to produce many species of photo-ions of the same element is a mix-blessing. It causes interferences but also provides ways for self-consistency tests. In favorable case, it can even enable us to analyze elements whose ionization potentials are too high but with molecules or radicals that are easier to ionize.
2. For vast majority of isotope ratios the short term reproducibility is good with one sigma less than 3% in most cases. So differential measurements relative to standards with same host minerals may be possible.
3. Hydrides and hydroxides are almost always present but can be reduced by pre-cleaning. However the isotope just 1 amu heavier than the major isotope usually suffers the biggest interference. We need to improve our mass resolution to resolve away their contribution.
4. For the more minor mass peaks we need the capability to increase the dynamic range of our detector. Fast beam or gain switching may be achievable with commercial components.

References:[1] Brownlee D. E. et al. (2004) Science, *304*, 1764-1769.

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