Application of RIMS to the Study of Beryllium Chronology in Early Solar System Condensates

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Resonant Ionization (RIMS) detection of Be decay products shows potential for addressing early solar system events.

### Lithium, Beryllium and Boron in the Early Solar System

Many unanswered questions remain concerning the timing, processes and conditions present in the early solar system. Short-lived ('extinct') nuclides can be useful in addressing early solar system events, but only after establishing an initial period of isotopic homogeneity for each isotopic system, as well as convincing evidence of closed system behavior, thereafter.

Be has potential as a recorder of early solar system events through two decay systems. ^{10}Be decays to ^{10}B with a half-life of 1.5 Ma, while ^{7}Be decays to ^{7}Li with a half-life of 35 days. All three elements are generally destroyed in stellar nucleosynthesis. ^{10}Be is formed in the solar system purely through energetic particle reactions. This

was likely a result of an energetic young sun [e.g., Shu F. H. et al. (1997) Science, 277, 1475–1479], although steady state production in the interstellar medium by galactic cosmic ray spallation with no stellar source has also been suggested [Desch S. J. et al. (2004) Astrophys. J., 602, 528–542].

Determination of the magnitude and extent of preserved ^{10}B excesses formed by decay of ^{10}Be, and possibly ^{7}Li excesses (from decay of ^{7}Be), can improve our understanding of the conditions and timescales of early solar system formation.

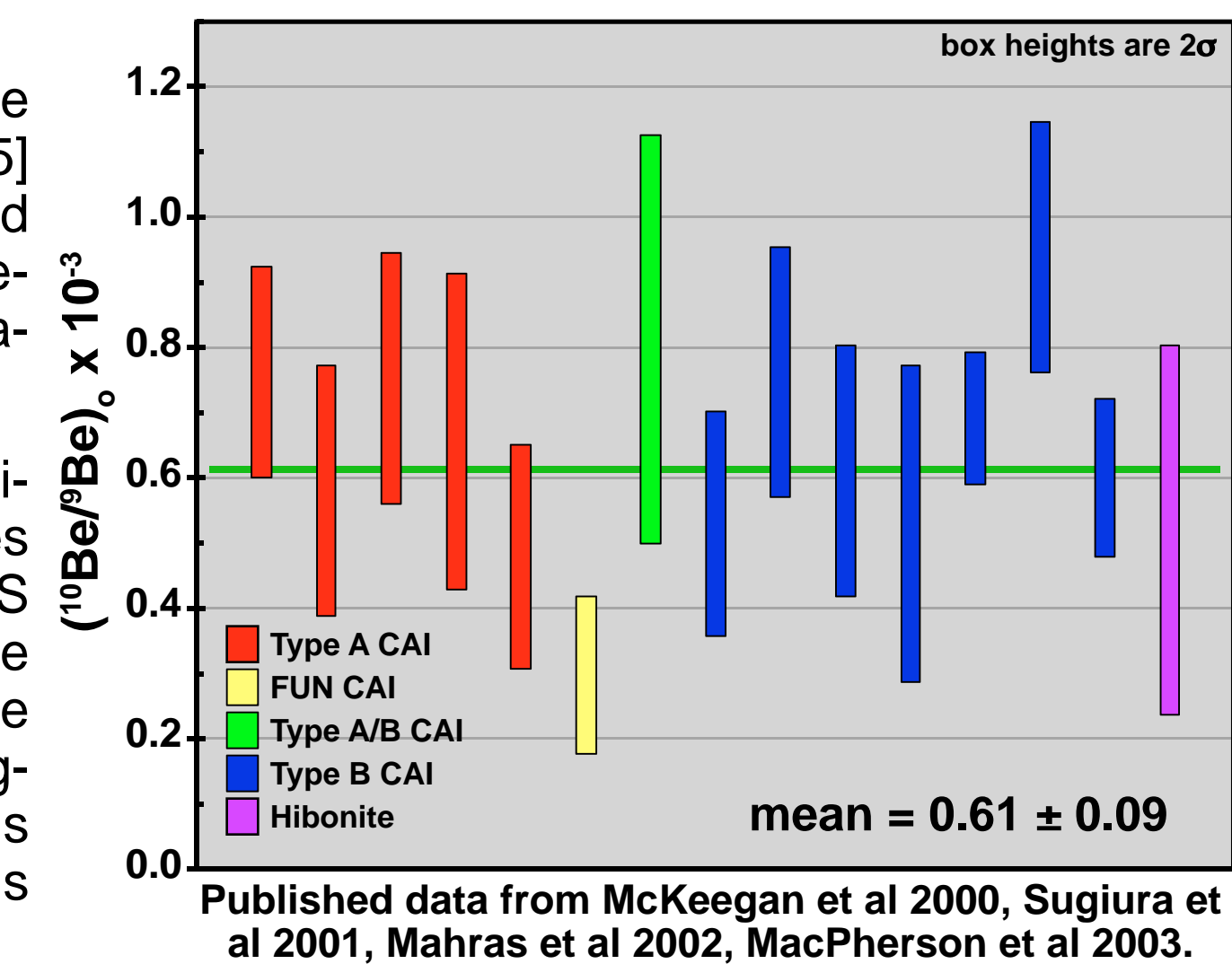|	Big Bang?	stellar nucleosynthesis?	supernovae?	energetic particle interaction?
^{6}Li	no	no	no	yes
^{7}Li	yes	yes	no	yes
^{7}Be	no	weak	yes	yes
^{9}Be	no	no	no	yes
^{10}Be	no	no	no	yes
^{10}B	no	no	no	yes
^{11}B	no	weak	yes	yes
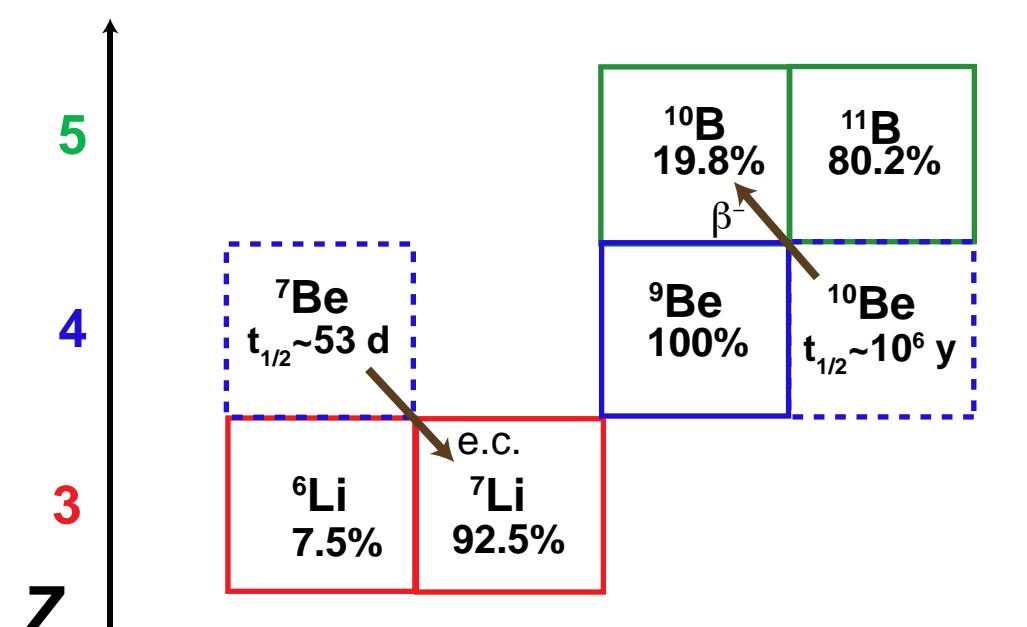
Beryllium Chronology in CAIs: The Evidence Thus Far

Secondary ionization mass spectrometry (SIMS) studies have focused on the short-lived decay of ^{10}Be to ^{10}B in early solar system condensates such as Ca-Al rich inclusions (CAIs). The presence of excess ^{10}B strongly suggests that these very refractory phases were witness to early solar system processes. Thus far, SIMS analyses yield generally good correlation between excess ^{10}B and Be/B within individual CAIs, and a general lack of correlation with the better established ^{26}Al-^{26}Mg decay system ($t^{1/2} = 7.3 \times 10^{5}$ y).

Reported detection of excess ^{7}Li resulting from the decay of ^{7}Be [Chaussidon M. et al. (2006) Geochim. Cosmochim. Acta, 70, 224-245] remains controversial. To make this determination, the authors needed lithium loss, excluding analyses suggesting lithium mobility. These results, if confirmed, would imply that some CAIs recorded particle irradiation events from the first days of the early solar system.

SIMS analyses use large analytical spot sizes (~30-50 um) and high primary beam currents to achieve adequate precision (±5%) on samples with low average concentrations of Be, B and Li (~10^{2} - 10^{3} ppb). SIMS useful yields for these elements (atoms detected/atoms consumed) are generally ~10^{-3}–10^{-4}. Pervasive terrestrial boron contamination and the high mobility of lithium create additional analytical complexity. Data suggest an inferred initial $^{10}Be/^{9}Be$ ratio in CAIs ~1.0×10^{-3}, and in FUN CAIs ~0.5×10^{-3}, but the reason for the scatter of initial isotopic ratios remains unclear, although initial isotopic heterogeneity remains one possibility.

Published data from McKeegan et al 2000, Sugiura et al 2001, Mahras et al 2002, MacPherson et al 2003.
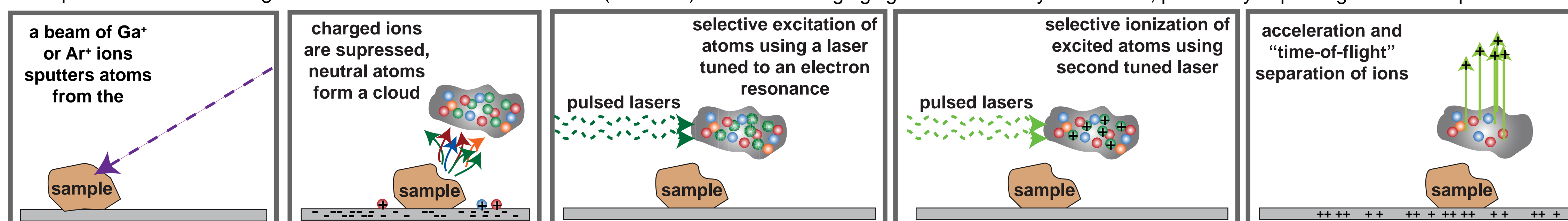
Resonant Ionization Mass Spectrometry

We are developing resonant ionization mass spectrometry (RIMS) methods aimed at the determination of B, Be and Li in early solar system materials such as Ca-Al-rich inclusions (CAIs) using the Chicago-Argonne Resonant Ionization Spectrometer for Mass Analysis (CHARISMA) instrument, designed for determination of trace element isotopic compositions with high spatial resolution [Savina, M. R. et al. (2003) Geochim. Cosmochim. Acta, 67, 3215-3225].
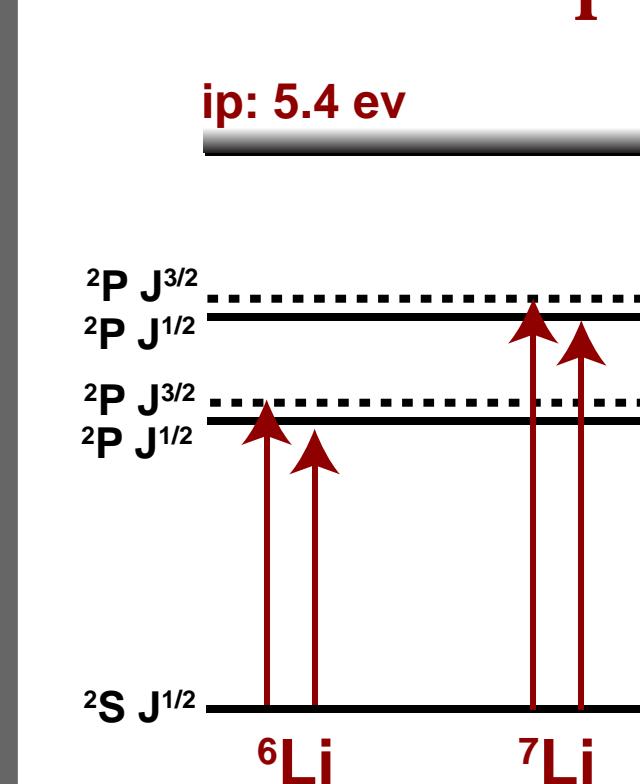
The advantages of RIMS lie in the ability to couple laser wavelengths with element-specific excited electronic states, combined with potentially small analytical spot sizes (<300 nm) and generally high useful yields (1-10%), thereby increasing the analytical precision at current spot sizes, or allowing analysis of smaller or lower concentration spots at comparable precision. A primary beam from an Ar+ or Ga+ ion gun (which can be narrowly focused down to 30 nm) or a focused laser beam is used to desorb neutral atoms from a sample surface. Secondary ions are suppressed, then neutral atoms of interest are selectively excited by one or more laser photons with wavelengths tuned to excite an intermediate (resonant) elec-

tronic state of the element of interest. This is followed by an additional laser photon with sufficient energy to ionize the excited atoms. This element-specific ionization minimizes isobaric interferences. The timing of each set of laser pulses sets the initial time for ion generation. Ions are then accelerated through a time-of-flight mass spectrometer and can be detected as analog or digital signals. Instrumental mass fractionation is monitored by bracketing samples with analyses of standards with similar elemental concentrations and known isotopic composition.

The CHARISMA instrument uses up to four Nd:YLF-pumped Ti:Sapphire lasers to generate tunable beams with wavelength ranges of ~700 nm to ~1000 nm. A non-tunable Nd-YAG laser with a fundamental wavelength of 1064.16 nm is also available. RIMS limitations include generally poor precision compared to SIMS, with isotopic differences smaller than ~10‰ difficult to resolve. Additionally, if lasers fail to saturate or nearly saturate the resonant steps in an excitation scheme, ion yields can be severely decreased and unstable isotopic fractionation can be introduced. Our current work is aimed at extending RIMS to these challenging light element analyses in CAIs, potentially improving on SIMS capabilities.

a beam of Ga+ or Ar+ ions sputters atoms from the sample

charged ions are supressed, neutral atoms form a cloud — pulsed lasers

selective excitation of atoms using a laser tuned to an electron resonance — pulsed lasers

selective ionization of excited atoms using second tuned laser

acceleration and "time-of-flight" separation of ions
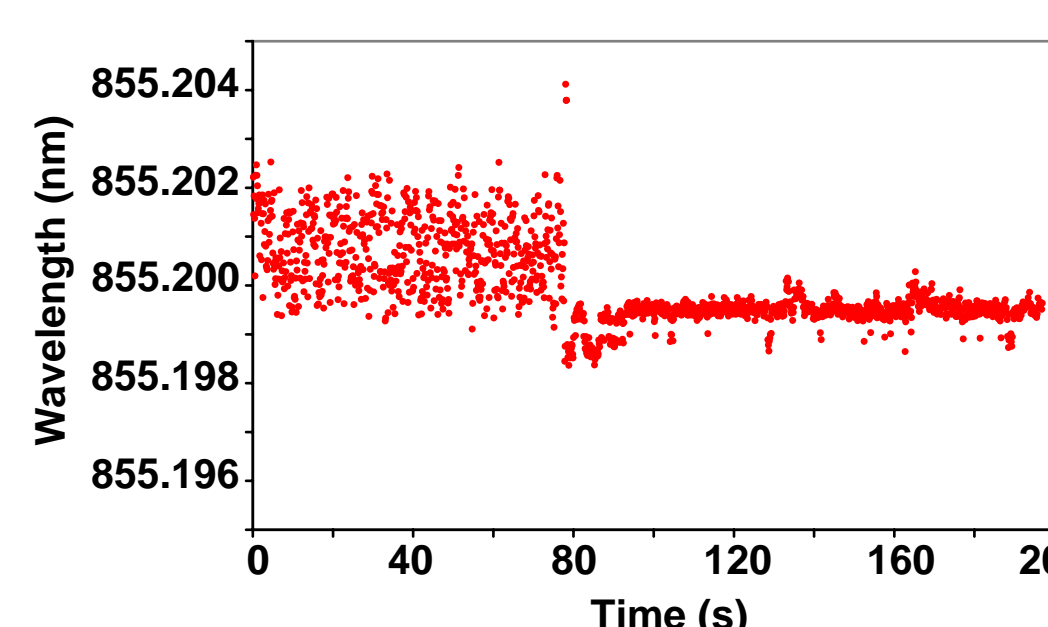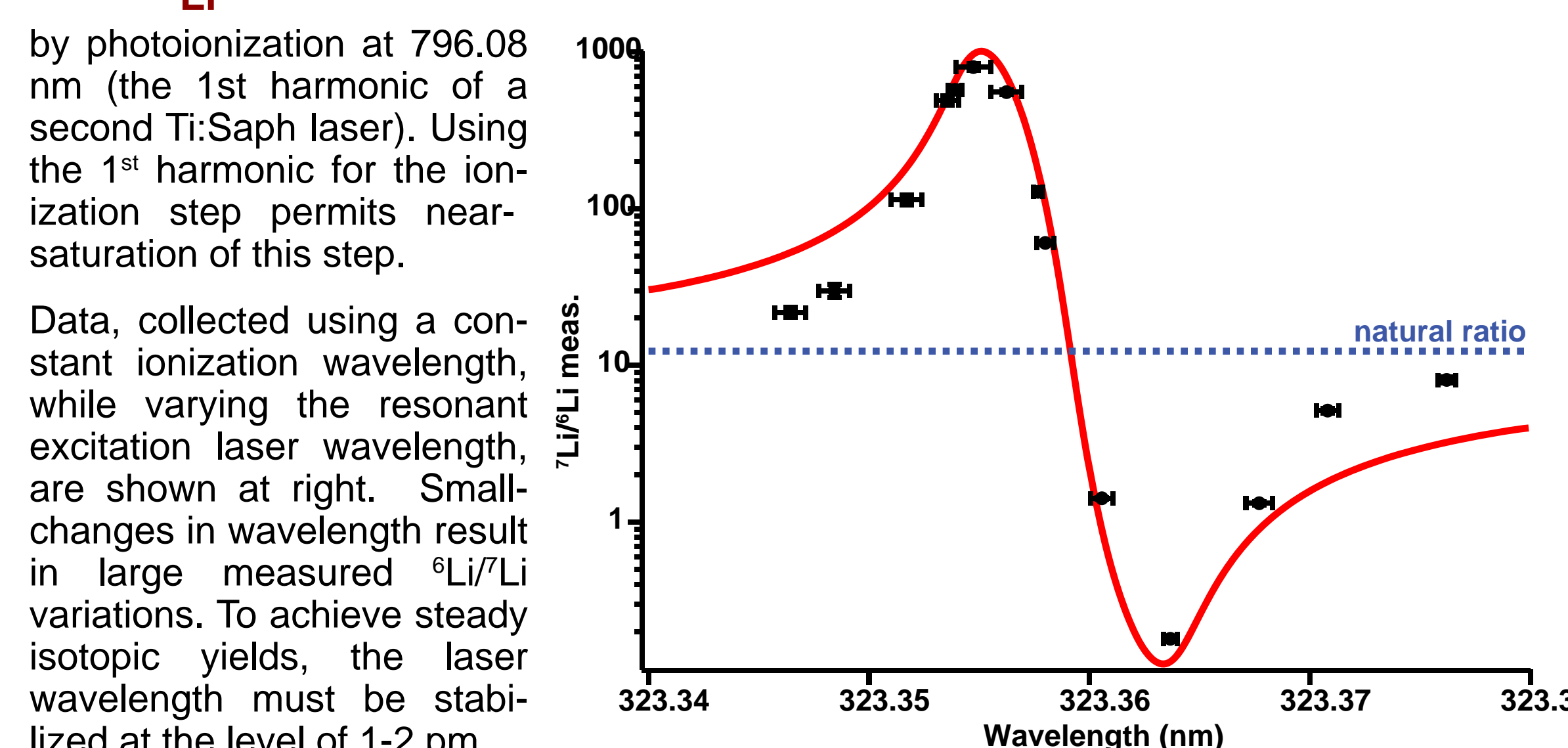
Isotope Shifts in Light Elements

While RIMS is, in principle, applicable to nearly all elements, appropriate laser ionization schemes can be challenging to develop and validate. We have used CHARISMA to develop resonant ionization schemes for Li, Be and B. The number of resonant states, and thus potential ionization schemes, for light elements such as Be, B and Li is limited by their simple electronic structures. In addition, low mass elements have large isotope shifts, i.e. different isotopes are resonant at slightly offset energies causing a 'splitting' of the resonance levels. In lithium, this shift translates into a 10 pm offset between ^{6}Li and ^{7}Li at the resonance of interest, easily resolved by our lasers.

ip: 5.4 ev

$^{2}P\ J^{3/2}$ 323.361 nm
$^{2}P\ J^{1/2}$ 323.362 nm
$^{2}P\ J^{3/2}$ 323.357 nm
$^{2}P\ J^{1/2}$ 323.356 nm
$^{2}S\ J^{1/2}$ ^{6}Li ^{7}Li

The above energy level diagram shows the isotopic and fine (J) splitting of lithium at one resonance under investigation. The fine splitting of the 2P states is much smaller than the isotopic splitting, and not resolvable with our wavelength resolution. Our laser bandwidth is typically ~4 pm, so small changes in laser wavelength can dramatically shift isotopic selectivity leading to a variance over 4 orders of magnitude in the measured $^{7}Li/^{6}Li$ ratio over a wavelength range of just 10 pm (see the Li RIMS section, below). Reliable determinations of Li isotope ratios (and, to a lesser extent, B isotopic ratios) is contingent on fine control of the laser wavelength.

Lithium RIMS

ip: 5.4 ev
796.08 nm (1H, 796.08 nm)
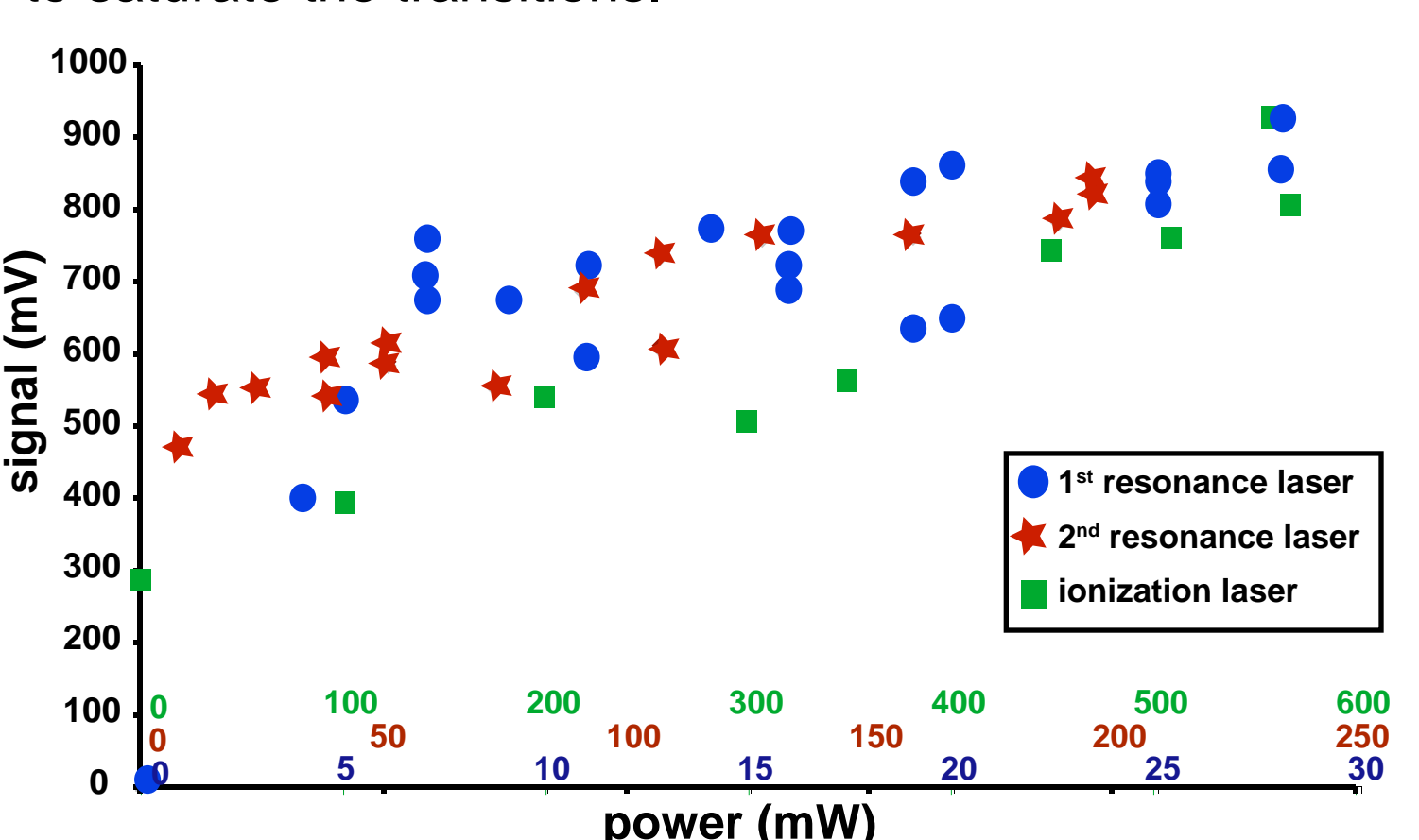^{2}P
323.36 nm (3H, 970.07 nm)
^{2}S
Li

Lithium resonant ionization exhibits the largest isotopic shift (as discussed above). We have focused on excitation schemes to assess the magnitude of the effect and to experiment with methods for achieving stable isotopic yields. One scheme investigated (see diagram at left) is a two-photon scheme, with excitation from the ground state to an intermediate level (^{2}S to ^{2}P) using a 323.36 nm photon (the 3rd harmonic of the Ti:Sapphire fundamental at 970.07 nm), followed

by photoionization at 796.08 nm (the 1st harmonic of a second Ti:Saph laser). Using the 1st harmonic for the ionization step permits near-saturation of this step.

Data, collected using a constant ionization wavelength, while varying the resonant excitation laser wavelength, are shown at right. Small changes in wavelength result in large measured $^{6}Li/^{7}Li$ variations. To achieve steady isotopic yields, the laser wavelength must be stabilized at the level of 1-2 pm.

We have recently achieved this level of stability by addition of interferometer feedback to the laser cavity. Results at left show the improvement in both laser wavelength stability, as well as laser bandwidth, when this feedback is used (at t=80 seconds). Laser wavelengths settle into a stable mode with sub-pico meter accuracy. We expect these improvements to permit useful lithium isotopic determinations in the near future.

Beryllium RIMS

ip: 9.3 ev
^{1}D 532.08 nm (2H, 1064.16 nm)
^{1}P 457.40 nm (2H, 914.79 nm)
234.93 nm (4H, 939.73 nm)
^{1}S
Be

Two resonant ionization schemes have been investigated for Be. The first is a two-photon scheme, with excitation from the ground state to an intermediate level (^{1}S to ^{1}P) using a 234.93 nm photon (the 4th harmonic of the Ti:Sapphire fundamental at 939.73 nm), followed by photoionization at 306.70 nm (the 3rd harmonic of 920.09 nm). The laser power was insufficient to saturate the

ionization step, however, producing low yields. We then developed a three-photon scheme using two resonant photons (energy level diagram at left), the first exciting the Be atom to a ^{1}P state, and the second with a wavelength of 457.40 nm (2nd harmonic of 914.79 nm) exciting to a ^{1}D state, from which the atom is ionized by a 532.08 nm photon (2nd harmonic of the Nd-YAG laser). Saturation curves (signal intensity as a function of laser power, shown below) show that the resonance lasers were able to saturate the transitions.


Simultaneous ionization and detection of Be and B was achieved on a standard glass sample with ppm concentrations of both elements, using five lasers. As in SIMS, the useful yields for these two elements are significantly different. The relative yield for Be was anywhere from 10 to 100 times higher than B.

Boron RIMS

ip: 8.3 ev
^{2}S 371.91 nm (2H, 743.82 nm)
249.75 nm (3H, 749.26 nm)
^{2}P $J^{3/2}$ $J^{1/2}$
B

Boron provides distinct resonant ionization challenges. These include a split ^{2}P ground state, with a low-lying J=3/2 state a mere 15.29 cm^{-1} above the J=1/2 ground state. We expect the two states to be equally populated in laser-desorbed B. We have achieved initial success using a two-color ionization scheme. The first excitation is ^{2}P to ^{2}S at 249.75 nm (3rd harmonic of 749.26 nm), followed by ionization with a 371.91 nm photon (2nd harmonic of 743.82 nm). The isotopic reproducibility is stable within analytical error (±10%) at high laser powers, but contributions from isotopic shifts have not yet been evaluated.

Below, two-color RIMS spectra for boron shows different combinations of the desorption, resonance, and ionization lasers (arbitrarily offset from one another by multiples of three units). Backgrounds are zero. The boron ion yield is only slightly enhanced with the addition of the ionization laser (compared with

two-photon resonance-only ionization), suggesting that the ionization step may not be saturated.

We are continuing to develop the boron resonant ionization scheme, exploring a three-photon scheme to excite both the B ground state and the low-lying J=3/2 state simultaneously. We expect to develop to improve the B useful yield by a factor of two or greater.
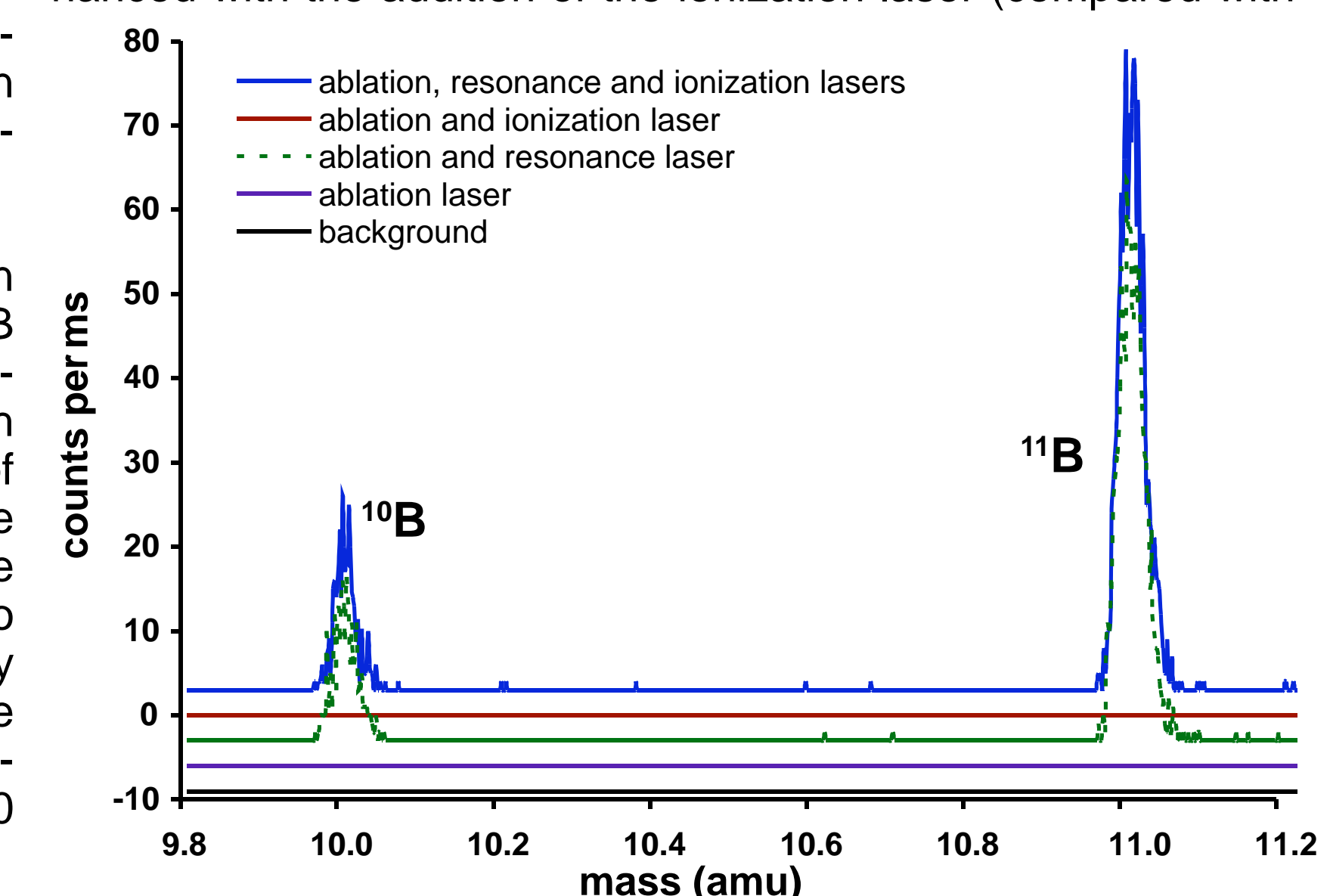
Conclusions

Our goal is to maximize useful yields for all three elements, demonstrate isotopic reproducibility for Be-B and Be-Li determinations on crystalline and glass samples, begin determinations on Allende CAIs analyzed in previous studies, and extend the Be-B record to chondrules. The ongoing improvements to laser wavelength stability are expected to contribute significantly to reaching this goal.