APPLICATION OF RIMS TO THE STUDY OF BERYLLIUM CHRONOLOGY IN EARLY SOLAR SYSTEM CONDENSATES.

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Introduction: Resonant ionization mass spectrometry (RIMS) is a technique only recently applied to problems in cosmochemistry. Thus far, RIMS has been used to characterize isotopic compositions of select trace elements including Ba, Mo and Zr in presolar grains, allowing the detection of preserved nucleosynthetic signatures of parent stars (*r*- and *s*-processes), as well as supernovae signatures [e.g., 1-4]. Unambiguous evidence for the presence of extinct technetium has also been reported in presolar grains [5]. We are currently developing RIMS methods aimed at the determination of B, Be and Li in early solar system materials such as Ca-Al-rich inclusions (CAIs) using two RIMS instruments designed, built and optimized for the determination of trace element isotopic compositions with high spatial resolution [6] at Argonne National Laboratory.

Applications In Be Chronology: Using secondary ionization mass spectrometry (SIMS) techniques, several recent studies have focused on the short-lived decay of ^{10}Be to ^{10}B ($t_{1/2} \sim 1.5$ Ma) [e.g. 7-11] in early solar system condensates. The presence of excess ^{10}B in these materials strongly suggests that CAIs and other highly refractory phases were witness to early system processes. ^{10}Be is likely to have formed in the solar system through energetic particle reactions, but steady state production in the interstellar medium by galactic cosmic ray spallation has also been suggested [12], with no stellar sources. The source of the initial ^{10}Be may be an active early sun (e.g., the x-wind model of [13]). Current data suggest that the inferred initial ^{10}Be/^{9}Be ratios in normal CAIs is $\sim 1.0 \times 10^{-3}$ and that the value in FUN CAIs is is $\sim 0.5 \times 10^{-3}$ [14, 15]. Also recently reported is the controversial detection of excess ^{7}Li resulting from the very short lived decay ($t_{1/2} \sim 53$ d) of ^{7}Be [11]. In order to make this determination, the authors modeled lithium loss, and excluded analyses suggesting lithium mobility. While the ^{7}Be results have not yet been confirmed, they require that some CAIs recorded particle irradiation events from the earliest solar system.

SIMS analyses use relatively large analytical spot sizes (~ 50 um) and high primary beam currents in order to achieve adequate precision ($\pm 5\%$) on samples with low concentrations of Be, B and Li (generally in the range of 10^2 - 10^3 ppb). SIMS useful yields for these elements (atoms detected/atoms consumed) are generally in the 10^{-3}–10^{-4} range [16]. Pervasive terrestrial boron contamination and the high mobility of lithium create additional analytical complexity. RIMS may be able to contribute further to understanding the magnitude and extent of ^{10}B excesses, and possibly ^{7}Li excesses, in early solar system materials by achieving higher useful yields, thereby increasing the analytical precision at the current spot sizes or allowing one to analyze smaller or lower concentration spots at comparable precision. RIMS can also be used to ionize and detect isotopes from more than one element simultaneously, permitting analyses of the same sample volume for multiple elements (rather than through successive ablation or sputtering steps).

Resonant Ionization Mass Spectrometry: 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 and generally large ion yields [6]. A primary beam from an Ar$^+$ or Ga$^+$ ion beam (which can be narrowly focused down to 30 nm) or a focused laser, is used to desorb neutral atoms from a sample surface. Atoms of interest in the resultant cloud of neutrals and ions are selectively excited by one or more laser photons tuned to intermediate (resonant) electronic states, followed by ionization from that state by an additional laser photon. This element-specific ionization greatly supresses isobaric interferences. The timing of each set of laser pulses sets the initial time for ions, which are then accelerated through a time-of-flight mass spectrometer. Instrumental mass fractionation is monitored by bracketed analyses of standards with similar elemental concentrations.

In addition to high spatial resolution and element-specific ionization, the Argonne RIMS instruments are optimized for high useful yields of 1-10%. Limitations include generally poor precision compared to SIMS. Isotopic differences smaller than ~ 10‰ are difficult to resolve. Additionally, if the lasers fail to saturate or nearly saturate the resonant steps in an excitation scheme, yields can be severely decreased and unstable isotopic fractionation can be introduced. While RIMS is in principle applicable to nearly all elements, appropriate laser ionization schemes can be challenging to develop and validate.

Developing RIMS-based Be Chronology: 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 nontunable Nd-YAG laser with a fundamental wavelength of 1064.16 nm is also available. Thus far, we have used this setup to develop resonant ionization

schemes for Be and B. The number of resonant states for light elements such as Be, B and Li is limited by their simple electronic structures.

Two resonant ionization schemes were investigated for Be. The first was a two-photon scheme, with excitation from the ground state to an intermediate level ($^1S \rightarrow ^1P$) 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. We then developed a three-photon scheme using two resonant photons, the first exciting the Be atom to the ^1P state, and the second with a wavelength of 457.40 nm (2nd harmonic of 914.79 nm) exciting it to a ^1D state from which it was subsequently ionized by a 532.08 nm photon (2nd harmonic of the Nd-YAG laser). Saturation curves (signal intensity as a function of laser power) showed that the resonance steps were saturated.

Boron provides different resonant ionization challenges. These include a split ^2P ground state, with a low-lying $J = 3/2$ state a mere 15.29 cm above the $J = 1/2$ ground state. The two states should be equally populated in laser-desorbed B. We have worked through several laser schemes to achieve initial success using a two-color ionization scheme. The first excitation is $^2P \rightarrow ^2S$ 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 was stable within analytical error (±10%) at high laser powers, but we were unable to saturate the ionization transition for this laser scheme (Fig. 1).

Simultaneous ionization and detection of Be and B was achieved on a standard glass sample with ppm concentrations of both elements, using all five lasers at once. 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. We speculate that this is due to B vaporizing as the oxide, in which case the desorption conditions will have to be adjusted to favor B atoms.

Development: We are continuing to develop the boron resonant ionization scheme. In particular, we will explore a three-photon scheme, exciting both the B ground state and the low-lying $J = 3/2$ state simultaneously. We expect this scheme to improve the B useful yield by a factor of two or more. 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. RIMS techniques for Be decay products show potential for addressing questions in early solar system history.

References: [1] Nicolussi G. K. et al. (1998) *Geochim. Cosmochim. Acta*, 62, 1093-1104. [2] Nicolussi G. K. et al. (1997) *Science*, 277, 1281-1283. [3] Savina M. R. et al. (2003a) *Geochim. Cosmochim. Acta*, 67, 3201-3214. [4] Barzyk J. G. et al (2006) *New Astron. Rev.*, 50, 587-590. [5] Savina M. R. et al. (2004) *Science*, 303, 649-652. [6] Savina, M. R. et al. (2003b) *Geochim. Cosmochim. Acta*, 67, 3215-3225. [7] McKeegan K. D. et al. (2000) *Science*, 289, 1334-1337. [8] Sugiura N. et al. (2001) *Meteoritics & Planet. Sci.*, 36, 1397-1408. [9] Marhas K. K. et al. (2002) *Science*, 298, 2182-2185. [10] MacPherson G. J. et al. (2003) *Geochim. Cosmochim. Acta*, 67, 3165-3179. [11] Chaussidon M. et al. (2006) *Geochim. Cosmochim. Acta*, 70, 224-245. [12] Desch S. J. et al. (2004) *Astrophys. J.*, 602, 528–542. [13] Shu F. H. et al. (1997) *Science*, 277, 1475–1479. [14] McKeegan K. D. and Davis A. M. (2007) In *Meteorites, Comets and Planets* (ed. A. M. Davis), *Treatise on Geochemistry* (ed. H. D. Holland and K. K. Turekian), 2nd edition, in press. [15] Liu M.-C. et al. (2007) this volume. [16] Hervig R. L. et al. (2006) *Chem. Geol.*, 227, 83-99.
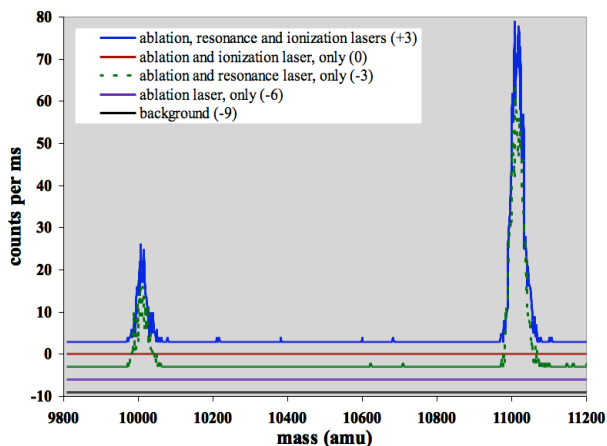
Fig. 1 Two-color RIMS spectra for boron showing different combinations of the desorption, resonance, and ionization lasers (arbitrarily offset from one another by multiples of three units). Backgrounds are zero. The boron ion yield is only slightly enhanced with the addition of the ionization laser (compared with two-photon resonance-only ionization), suggesting that the ionization step may not be saturated.