ANALYSIS OF STRONTIUM, ZIRCONIUM, MOLYBDENUM, AND BARIUM ISOTOPES IN PRESOLAR SILICON CARBIDE GRAINS WITH CHILI. T. Stephan[1,2], R. Trappitsch[1,2], P. Boehnke[1,2], A. M. Davis[1,2,3], M. J. Pellin[1,2,3,4], and O. S. Pardo[1,2], [1]Department of the Geophysical Sciences, The University of Chicago, Chicago, IL 60637, USA, [2]Chicago Center for Cosmochemistry, [3]The Enrico Fermi Institute, The University of Chicago, Chicago, IL 60637, USA. [4]Materials Science Division, Argonne National Laboratory, Argonne, IL 60439, USA, (tstephan@uchicago.edu)

Introduction: We have measured Sr, Zr, Mo, and Ba isotopes in presolar SiC grains using CHILI, the Chicago Instrument for Laser Ionization [1]. This continues a preliminary study in which we successfully measured Sr and Ba in 10 out of 22 presolar SiC grains, including three X grains [2–4]. Zr, although searched for, was not detected in any of the previously investigated grains. However, with a technically improved CHILI, we were able to measure Zr in presolar SiC grains. In addition, we analyzed Mo, another element that is particularly important for understanding the *s*-process in asymptotic giant branch (AGB) stars [5,6].

Samples: Thirty-one presolar SiC grains from the 1.5–3 µm size separate (KJG), extracted from the Murchison CM2 meteorite more than 20 years ago [7] and mounted on gold foil, were analyzed in this study. In contrast to recent work on SiC grains [8–12], the samples in this study were not additionally treated with concentrated acids to remove parent-body and terrestrial contamination. Energy dispersive X-ray images of the mount were acquired in a scanning electron microscope to locate SiC grains on the mount.

RIMS analysis: CHILI is a resonance ionization mass spectrometry (RIMS) instrument, which is equipped with six tunable Ti:sapphire lasers. This allows simultaneous resonance ionization of three elements with independent two-photon ionization schemes. All six laser beams with different wavelengths are brought onto a single line before entering the analysis chamber. Using a broadband mirror, the laser beams are reflected so that they travel twice through a cloud of neutrals, which were desorbed from the sample by a 351 nm Nd:YLF laser beam, focused to ~1 µm onto the center of the respective grain.

We first measured 15 grains simultaneously for their Sr, Zr, and Ba isotopes and then 18 grains for Sr, Mo, and Ba, including two grains that had been measured for Sr, Zr, and Ba. We used previously developed ionization schemes (Table 1). Only the Zr scheme (Table 1) was slightly modified after performing a wavelength scan for the second (ionization) step laser. This increased the sensitivity by 25–30 %. Another increase in Zr sensitivity was achieved by replacing some mirrors, bringing the combined laser beams into the analysis chamber, with mirrors that have higher reflectance especially at lower wavelength, important for the first (excitation) step (296.172 nm) in the Zr scheme. The analytical precision for Sr, Zr, and Ba was increased, compared to the preliminary study [2–4], due to various improvements in the time-of-flight mass spectrometer, ionization laser system, desorption laser stability, and instrument control and data collection software.

Single-shot data were recorded and corrected for dead time effects [1,14]. Standards (Table 1), which were assumed to be of normal terrestrial isotopic composition, were used for correction of mass-dependent and non-mass-dependent isotope fractionation [1].

Table 1: Resonance ionization schemes and standards

	λ_1 [nm]	λ_2 [nm]	Ref.	Standards
Sr	460.862	405.214	[10]	SRM 855a[1]
Zr	296.172	442.575	[6][2]	Zr metal
Mo	313.350	388.337	[6]	SRM 855a, 1264a[3]
Ba	307.247	883.472	[13]	$BaTiO_3$

[1]NIST SRM 855a (180 ppm Sr and noncertified Mo)
[2]modified for λ_2 from 442.533 nm in reference [6]
[3]NIST SRM 1264a with 0.49 wt% Mo

Results: All 31 investigated SiC grains showed detectable amounts of all elements the ionization lasers were tuned for in the respective measurement. Meaningful isotope ratios, which showed deviations from terrestrial values beyond 3σ at least for one isotope ratio in one element, were found for 26 grains. Nine out of 31 grains had anomalies beyond 3σ in Sr, five out of 15 grains in Zr, 16 out of 18 grains in Mo, and 16 out of 31 grains in Ba. All isotope results are shown in Fig. 1 as δ-values (deviation from terrestrial ratio in ‰). Figure 2 shows three-isotope plots for Mo in comparison with literature data [6]. A striking observation is that the analytical precision is much higher than in the earlier study.

Discussion: All isotope patterns shown in Fig. 1 are consistent with mainstream SiC grains formed in low-mass AGB stars [5,9,10,15]. The pure *s*-process isotopes ^{86}Sr, ^{87}Sr, ^{96}Mo, ^{134}Ba, and ^{136}Ba are relatively enriched, whereas isotopes dominated by *p*-process (^{84}Sr, ^{92}Mo, ^{94}Mo, ^{130}Ba, ^{132}Ba) and *r*-process (^{96}Zr, ^{100}Mo, ^{135}Ba) show the strongest depletions. The neutron-magic ^{88}Sr is also mostly of *s*-process origin and therefore only slightly depleted. Branch points at ^{89}Sr, ^{90}Sr, and ^{91}Y and the strength of the ^{13}C pocket ultimately determine the relative abundances of the various Zr isotopes [5]. ^{93}Zr with its 1.61 Ma half-life behaves as a stable isotope during *s*-process. Mo is an ideal element for this kind of study. Resonance ionization is very effective for this element, which has seven stable isotopes (two *p*-only, one *s*-only, and one *r*-only isotope) with terrestrial abundances between 9 and 24 %. The relative abundances of $^{95-98}$Mo depend on the branch point at ^{95}Zr [5]. The relative abundances of $^{134-138}$Ba mostly depend on the branch point at ^{134}Cs [5].

Conclusions: For the first time, three elements have been successfully analyzed simultaneously in presolar SiC grains with CHILI. Besides Sr and Ba, which have been analyzed in SiC with CHILI before, we have added Zr and Mo as possible choices for these measurements. Mo showed the most promising results with regard to analytic precision, surpassing previous measurements with RIMS. The results will help to further constrain models of the *s*-process in low-mass AGB stars.

References: [1] Stephan T. et al. (2016) *Int. J. Mass Spectrom., 407,* 1–15. [2] Stephan T. et al. (2015) *LPS 46,* Abstract #2825. [3] Stephan T. et al., (2016) *MAPS, 51,* Abstract #6402. [4] Stephan T. et al. (2017) *GCA,* submitted. [5] Lugaro M. et al. (2003) *ApJ, 593,* 486–508. [6] Barzyk J. G. et al. (2007) *MAPS, 42,* 1103–1119. [7] Amari S. et al. (1994) *GCA, 58,* 459–470. [8] Levine J. et al. (2009) *Int. J. Mass Spectrom. 288,* 36–43. [9] Liu N. et al. (2014) *ApJ, 786,* 66. [10] Liu N. et al. (2015) *ApJ, 803,* 12. [11] Trappitsch R. et al. (2016) *MAPS, 51,* Abstract #3025. [12] Trappitsch R. et al. (2017) *GCA,* submitted. [13] Savina M. R. et al. (2003) *GCA, 67,* 3215–3225. [14] Stephan T. et al. (1994) *J. Vac. Sci. Technol. A, 12,* 405–410. [15] Liu N. et al. (2014) *ApJ, 788,* 163.

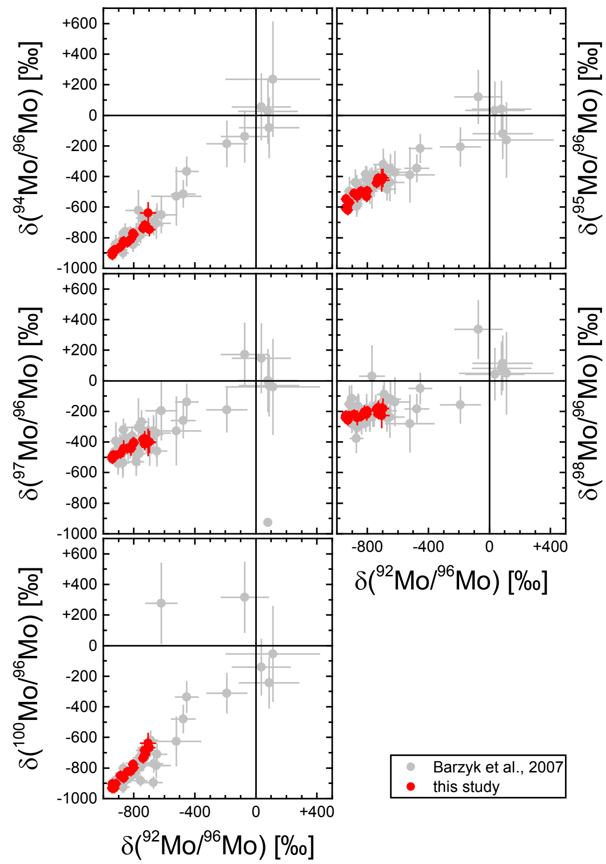

Fig. 2: Three-isotope plots for Mo for 16 grains from this study in comparison with literature data [6]. Uncertainties are 2σ.

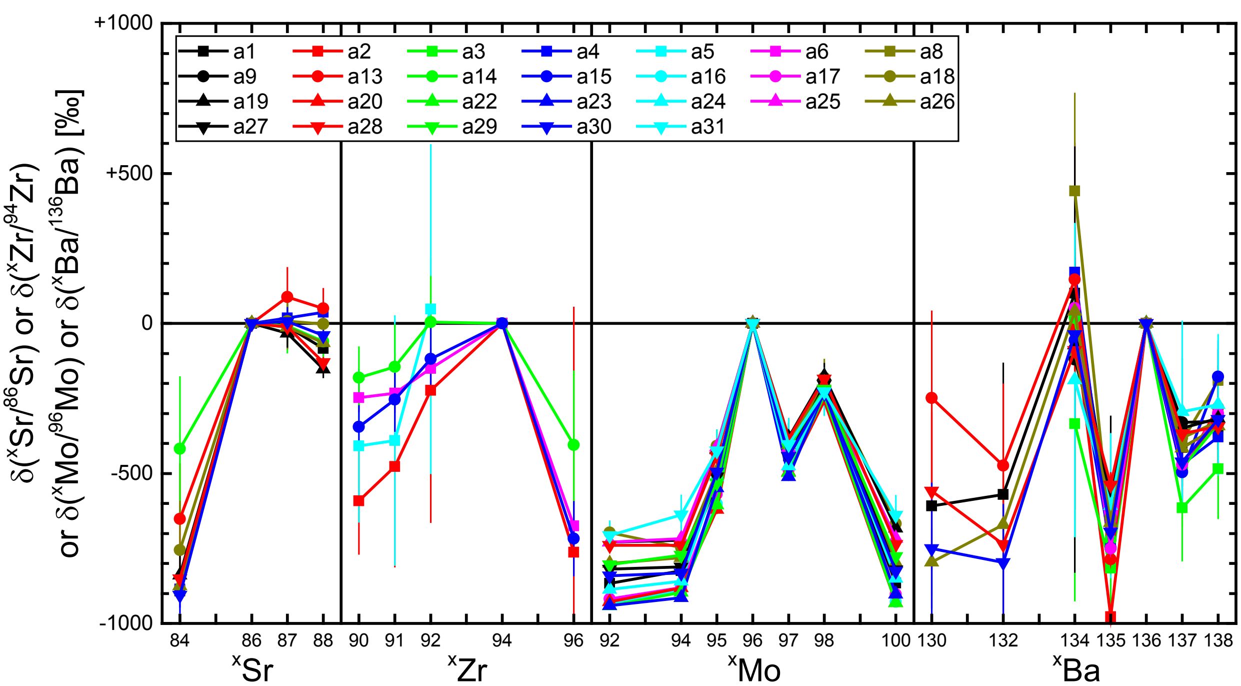

Fig. 1: Isotope patterns for Sr, Zr, Mo, and Ba measured in presolar SiC grains using CHILI. Uncertainties are 2σ.