TRACE ELEMENT RATIOS WITH CHILI: A PROGRESS REPORT. A. Regula[1,2], H. E. Bloom[1,2], N. Dauphas[1,2,3], A. M. Davis[1,2,3], J. M. Korsmeyer[2,4], M. J. Krawczynski[5], T. Stephan[1,2], [1]Department of the Geophysical Sciences, The University of Chicago, Chicago, IL, USA, [2]Chicago Center for Cosmochemistry, [3]Enrico Fermi Institute, The University of Chicago, Chicago, IL, USA, [4]Department of Chemistry, The University of Chicago, Chicago, IL, USA, [5]Department of Earth and Planetary Sciences, Washington University in St. Louis, St. Louis, MO, USA. E-mail: regula@uchicago.edu.

Introduction: Currently, the dominant techniques for in-situ trace element analysis are laser ablation inductively coupled plasma mass spectrometry (LA-ICPMS), secondary ion mass spectrometry (SIMS), and electron beam techniques. While LA-ICPMS and SIMS offer low detection limits, both techniques suffer from potential isobaric interferences on elements present in trace concentrations. LA-ICPMS and SIMS are also destructive techniques and have relatively low useful yields. Electron beam techniques offer high spatial resolution and a non-destructive means of analysis but suffer from high detection limits. Resonance ionization mass spectrometry (RIMS) offers the potential for analysis of elements at trace concentrations, with high useful yield, and without the same potential for isobaric interferences as SIMS and LA-ICPMS. The Chicago Instrument for Laser Ionization (CHILI) uses RIMS to measure the isotopic compositions of small samples at high spatial resolution and high sensitivity [1]. CHILI should be able to measure trace element ratios, but so far has not been extensively applied to such problems.

In order to present meaningful trace element ratios, it is important to quantify the relative sensitivity factor (RSF) for a ratio. The RSF is the ion/ion ratio of two elements, measured by CHILI, divided by the "true" atom/atom ratio of those elements, taken from reliable measurements in the literature.

Matrix effects can be problematic in SIMS analysis, where a material's matrix composition can have an effect on the element-specific ionization efficiency. It has long been claimed that RIMS avoids this problem, however this assertion still needs testing.

To demonstrate the utility of CHILI for measuring trace element ratios, we have selected seven well-characterized iron meteorites (six of group IVB and one of group IIAB) for trace element analysis; two group IVB meteorites had already been analyzed in preliminary work [2]. LA-ICPMS and solution isotope dilution negative thermal ionization mass spectrometry (NTIMS) were used to determine the bulk concentrations of the highly siderophile elements (HSE) in these iron meteorites [3, 4, 5]. Here, we present Ru/Mo RSFs measured using CHILI from the group IVB iron meteorites Tlacotepec, Skookum, Cape of Good Hope, Santa Clara, Tawallah Valley, and Hoba, and the group IIAB iron meteorite Coahuila.

Materials and Methods: Polished sections of each meteorite were imaged via SEM prior to analysis with CHILI. CHILI works via RIMS, where neutral atoms (as well as molecules and secondary ions) are desorbed from a target surface, and atoms of two or three target species are ionized by lasers tuned to element-specific wavelengths targeting electronic transitions. Either a 351 nm desorption laser or a Ga^+ ion gun can be used to release neutral atoms. CHILI can currently analyze materials at lateral resolutions of ~1 µm and with very low detection limits. Moreover, as CHILI ionizes neutral atoms desorbed or sputtered from the target surface, which represent the majority of particles generated, it should not be subject to the same matrix effects as SIMS instruments are.

Table 1: Literature compositions and CHILI-generated RSFs for iron meteorites analyzed in this study. Errors where reported are 1σ standard deviations.

Meteorite	Tlacotepec	Skookum	Cape of Good Hope	Santa Clara	Tawallah Valley	Hoba	Coahuila
Mo (ppm)[1]	23.9±0.5	32.8±0.7	22.2±1.1	31.0±0.6	32.9±0.9	24.6±0.4	6.66±0.16
Ru (ppm)[1]	29.8±0.3	23.8±0.3	29.4±0.3	24.9±0.5	24.0±0.5	29.2±0.3	19.86±0.89
Ru/Mo (atoms/atoms)	1.320±0.031	0.768±0.019	1.402±0.071	0.850±0.024	0.772±0.027	1.256±0.024	3.16±0.16
RSF_{DL}[2]	$0.223^{+0.012}_{-0.011}$	$0.244^{+0.023}_{-0.021}$	$0.240^{+0.031}_{-0.028}$	$0.283^{+0.023}_{-0.021}$	$0.258^{+0.037}_{-0.033}$	0.261±0.007	$0.276^{+0.057}_{-0.047}$
# of data points	25	26	13	6	7	6	7
RSF_{IG}[3]	$0.338^{+0.047}_{-0.042}$	$0.305^{+0.060}_{-0.050}$	$0.265^{+0.018}_{-0.017}$	$0.280^{+0.029}_{-0.026}$	$0.272^{+0.042}_{-0.037}$	0.268±0.008	$0.289^{+0.035}_{-0.031}$
# of data points	21	20	6	6	6	6	4

[1]Literature values from [3] except for Coahuila [4]
[2]DL refers to measurements with the desorption laser
[3]IG refers to measurements with the ion gun

The Ru/Mo ratio was measured in each meteorite using both CHILI's desorption laser and ion gun to compare the results of each technique. For each meteorite, a minimum of four spectra with both the laser and ion gun were measured, taken in areas of plessitic matrix across the surface of the mount. Kamacite spindles and plessite matrix, where they appear, show identical Ru/Mo ratios [2], so the latter should be representative of bulk meteorite Ru/Mo ratios. Each spectrum represents 10^6 shots of the laser or gun rastered over a 10×10 μm^2 area. As isotopes of Ru and Mo share the same mass at 96 u, 98 u, and 100 u, we employed an alternate shot firing scheme during analysis. Lasers for Ru and Ba were fired on alternate shots with the Mo lasers. Although this reduces the useful yield by 50%, it allows us to clearly separate the Ru and Mo signals. No Ba signal was seen in the meteorites, as it is a highly lithophile element.

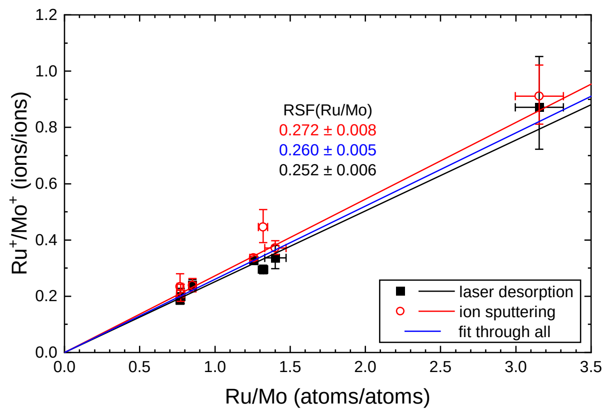

Figure 1: CHILI-derived Ru/Mo ionic ratio values plotted against meteorite Ru/Mo ratios from [3, 4]. RSF values are the slopes of the regression lines calculated through the datapoints. Error bars are 1σ standard deviations.

Results: Ru/Mo RSFs generated from each meteorite are presented in Table 1, as well as the Ru and Mo concentrations and Ru/Mo ratios for each meteorite [3, 4]. RSF values for the laser and gun data were generated via regression through a plot of the CHILI-derived Ru/Mo ionic ratios vs. literature Ru/Mo ratios (Fig. 1), where the slope of the line represents the RSF.

Discussion: RSFs were found not to vary significantly with composition (e.g., meteorite Ni wt%, Fig. 2) in the existing dataset. This is promising, as it shows consistency in CHILI's sensitivity to the Ru/Mo ratio through materials with a range of compositions.

The RSFs calculated from the laser and ion gun measurements were generally similar.

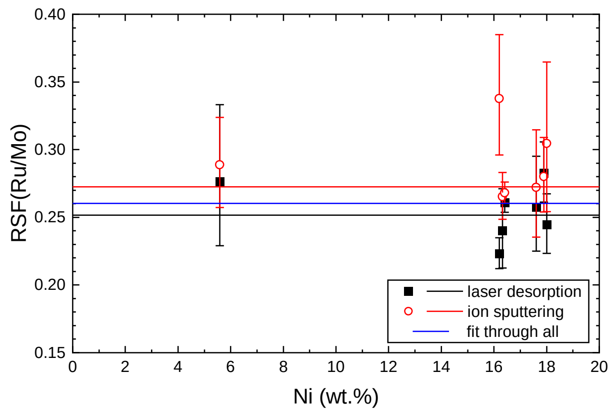

Figure 2: RSF values plotted against meteorite Ni concentrations from [5]. Error bars are 1σ standard deviations.

Future work will include analysis of materials with lower trace element concentrations in order to expand the range of applicability of CHILI, and could also include additional meteorites of more varied bulk composition to further confirm consistency of calculated RSF values.

References: [1] Stephan T. et al. (2016) *Int. J. Mass Spectrom.*, *407*, 1–15. [2] Regula A. et al. (2021) *MAPS*, *56*, A227 (#6287). [3] Campbell A. J. and Humayun M. (2005) *GCA*, *69*, 4733–4744. [4] Walker R. J. et al. (2008) *GCA*, *72*, 2198–2216. [5] Petaev M. I. and Jacobsen S. B. (2004) *MAPS*, *39*, 1685–1697. [6] Buchwald V. F. (1975) *Handbook of Iron Meteorites*, *University of California Press*, 1426 pp.