TOWARD TRACE ELEMENT CONCENTRATIONS WITH CHILI

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Introduction: The Chicago Instrument for Laser Ionization (CHILI) was designed to measure the isotopic compositions of small samples at high spatial resolution and high sensitivity [1]. CHILI utilizes resonance ionization mass spectrometry (RIMS): Neutral atoms (as well as molecules and secondary ions) are desorbed from a target surface, and atoms of two to three target species are ionized by Ti:sapphire lasers tuned to element-specific wavelengths targeting electronic transitions. CHILI can currently analyze materials at lateral resolutions of ~1 µm and with very low detection limits. The capabilities of CHILI lend themselves to measurement of ratios of trace element concentrations, but CHILI has yet to be applied to such problems.

In preparation for future trace element partitioning experiments, we have selected two well-characterized iron meteorites for trace element analysis. Laser ablation inductively coupled plasma mass spectrometry (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 iron meteorites [2, 3]. Partitioning of some elements between kamacite and taenite has been investigated [4], with taenite showing a preference for the HSE Au and Re. Zoning of some of the HSE on the scale of 10–20 µm has also been studied [5], finding similarly elevated HSE contents in taenite. These previous efforts lay the groundwork to which we can compare the results of our analysis and potential future measurements. Here, we present CHILI measurements of the Ru/Mo ratio of the group IVB iron meteorites Tlacotepec and Skookum.

Materials and Methods: We imaged polished sections of Tlacotepec and Skookum via scanning electron microscopy (SEM) and selected regions of interest on both. A region of Tlacotepec that seemed representative of the average material was selected and nine points were analyzed. For Skookum, a region was chosen that contains both plessitic matrix and kamacite crystals. Here, we analyzed six points on a transect roughly 45 µm across, two points each on either side of a 60 µm × 10 µm kamacite grain, and two within the grain. The lasers for Ru and Ba (the third element to which CHILI is currently tuned) were fired on alternate desorption laser shots from the Mo lasers as Ru and Mo both have isotopes at 96 u, 98 u, and 100 u. Although this reduces the useful yield by 50%, it allows us to clearly discern the Ru and Mo signals. No Ba signal was seen, as this is a highly lithophile element.

Results: The Ru/Mo RIMS ion ratios for our nine analysis points on Tlacotepec range from 0.214 to 0.246, with an average of 0.230±0.009 (1σ standard error). The ratio for Skookum ranges from 0.138 to 0.174, with an average of 0.161±0.013. From the six analysis points, no systematic difference in the Ru/Mo ratios between the plessitic matrix and the kamacite grain was detected. Calculating atomic Ru/Mo ratios using data from [2] yields values of 1.266 and 0.664 for Tlacotepec and Skookum, respectively. The same exercise with data from [3] yields ratios of 1.320 and 0.768. Our values reproduce the higher Ru/Mo in Tlacotepec vs. Skookum measured in previous studies, although the absolute ratios are not the same. Calculating a relative sensitivity factor (RSF) from Tlacotepec data, assuming literature data represents the true ratios, we can apply the same RSF to our results from Skookum. The measured ratios for Skookum using the RSF calculated from [2] or [3] are 33 % or 20 %, respectively, higher than the literature values.

Discussion: The discrepancy between our RIMS data and the LA-ICPMS data is presently not understood but might be due to the vast difference in volume of the analyzed material. We have so far only analyzed a relatively small region in each sample that may not be representative of the bulk composition. Further analyses are required to detect possible heterogeneities within those meteorites.

These data represent the first promising steps on the path of applying CHILI to measuring trace element ratios. Combined with appropriate well-characterized standard materials, CHILI should prove useful for measurement of low-concentration elements of interest at spatial scales of a few µm.

References: [1] Stephan T. et al. (2016) *International Journal of Mass Spectrometry* 407:1–15. [2] Campbell and Humayun (2005) *Geochimica et Cosmochimica Acta* 69:4733–4744. [3] Walker et al. (2008) *Geochimica et Cosmochimica Acta* 72:2198–2216. [4] Rasmussen et al. (1988) *Meteoritics and Planetary Science* 23:107–112. [5] Campbell and Humayun (1999) *Analytical Chemistry* 71: 939–956.