CHILI – THE CHICAGO INSTRUMENT FOR LASER IONIZATION – A PROGRESS REPORT.

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Introduction: Every increase in lateral resolution of analytical instruments in the past has enabled new discoveries. For example, in presolar grain research, high resolution techniques led to the finding of subgrains in presolar graphite [1], the measurement of elemental and isotopic heterogeneities in presolar SiC [2–4], and the in-situ detection of presolar silicates in interplanetary dust particles [5]. High resolution SIMS (secondary ion mass spectrometry) techniques like NanoSIMS [6] and TOF-SIMS (time-of-flight SIMS) [7] played a vital role in some of these discoveries.

In 2006, the Stardust mission [8] returned two types of extraterrestrial samples that also call for high resolution analytical techniques: dust from comet 81P/Wild 2 [9] as well as contemporary interstellar dust, though the latter still awaits verification [10]. Presolar grains in Wild 2 samples are sub-micrometer in size [11, 12], just at the edge of the capability of present-day SIMS techniques. Contemporary interstellar dust particles are expected to be of a similar size range [13].

With the decrease in sample size, the number of atoms in the analyzed volume becomes a major limiting factor. Therefore, an increase in lateral resolution by simply reducing the diameter of the analytical beam is not sufficient. When it comes to trace elements, an increase in useful yield – the ratio between detected and consumed atoms from a sample – is imperative.

In SIMS, the useful yield is often limited by the fraction of secondary particles that are released as ions. Even in favorable cases, this fraction rarely exceeds 1 %. Limitations in instrument transmission and detection efficiencies further reduce the useful yields.

More than 99 % of secondary particles, most of which are neutral atoms, are not ionized in the sputtering process. These atoms can be efficiently ionized with lasers tuned to resonances.

Resonant Ionization Mass Spectrometry (RIMS): In RIMS, atoms removed by ion sputtering or laser desorption are intercepted by multiple pulsed laser beams that are tuned to excite successive electronic transitions in an element of interest and finally to ionize those atoms from their excited state. The photoions are mass separated, in, *e.g.*, a time-of-flight mass spectrometer. More than one element can be ionized if the number of lasers is increased to realize several ionization schemes simultaneously. Since the ionization process is highly element-specific, instrumental mass resolution is not critical if the elements don't have isobaric interferences.

In addition to resonant ionization, secondary neutrals can be nonresonantly ionized via single photons using a VUV F_2 excimer laser. Since this process is not element-specific, mass resolution becomes important.

CHILI: The next generation RIMS instrument is presently under construction at the University of Chicago [14]. The new instrument is named CHILI (Chicago Instrument for Laser Ionization) and builds on the success of two instruments of similar design, CHARISMA [15] and SARISA [16]. While the former pioneered isotopic measurements of trace elements like Cr, Sr, Zr, Mo, Ru, and Ba in presolar SiC grains [17–22], the latter is mainly used to measure depth profiles of trace elements in Genesis solar wind collectors [23].

The main features that distinguish CHILI from its two predecessors are significant increases in lateral and mass resolution as well as in sensitivity, which required major changes in design as described here.

Liquid metal ion gun. To achieve maximum lateral resolution, a new Ga liquid metal ion gun will be used that can be focused to a few nanometers. Such guns were recently developed mainly for focused ion beam (FIB) sample preparation tools. Despite their little ionization efficiency –an advantage for RIMS – Ga liquid metal ion guns have been widely used in SIMS to achieve high lateral resolution. However, a further substantial increase in lateral resolution cannot be accomplished with ion sputtering, since even an infinitesimal beam diameter causes a collision cascade that releases secondary particles from an area several nm in size.

Laser ionization. As in CHARISMA and SARISA, tunable Ti:sapphire lasers for resonant ionization will be used in CHILI. It is planned to have initially four such lasers, which should allow to analyze isotopes of two elements simultaneously. To minimize reflective loss, all entrance windows for bringing the laser beams into the vacuum chamber will be tilted at Brewster's angle. In addition to the Ti:sapphire lasers, an F_2 excimer laser for nonresonant ionization will be used mainly for measuring trace element abundances.

Mass spectrometer. For SARISA, major improvements in ion optical design compared to CHARISMA led to an increase in useful yield from ~2 % to ~25 %. By increasing the acceleration voltage for the photoions from 1 kV in SARISA to 9 kV in CHILI, the efficiency of ion extraction will be further increased and the detection probability will be improved. In addition, an improvement in mass resolution by a factor of three can be anticipated. The 40–50 % useful yield aimed for is mainly limited by the ~60 % active surface area of the microchannel plate detector, leaving not much room for further improvement.

Ion counting. In most current instruments, counting statistics limits the dynamic range, because most detectors cannot accurately count more than one ion per time channel for one ionization pulse. To avoid major dead time corrections that would increase uncertainties [24], count rates are typically limited to 0.1 counts per pulse for the most abundant ion species. For CHILI, a multi-anode microchannel plate detector that should be able to distinguish multiple ions per pulse will be developed. In addition, the repetition rate for the laser ionization should be increased from 1 to perhaps 10 kHz to improve counting statistics.

Mechanical design. The general design of CHILI was changed compared to SARISA to a vertical flight tube sitting above the sample chamber that is mounted on an H-shaped laser table with active piezoelectric vibration isolators (Figure). Great emphasis was put on creating a rigid structure that should minimize relative motion of the various parts – sample, ion gun, lasers – and is isolated as a whole from possible sources of vibration. The sample will sit horizontally on a recently finished piezoelectric driven stage that provides sub-micrometer reproducibility. A newly designed sample holder will hold samples up to ~45×65 mm^2 in size.

Vacuum system. In order to achieve ultra-high vacuum conditions (<10^{-9} hPa) in the analysis chamber, a new system was designed using magnetically levitated turbomolecular pumps with special vibration isolation. Analysis and sample transfer chambers have independent pumping systems where each turbomolecular pump is backed up by a drag pump, a small turbomolecular pump that withstands relatively high forevacuum pressures up to 18 hPa. The drag pumps are backed up with reservoir volumes that only need to be evacuated once per day. Therefore, the scroll pumps only run for a few minutes per day, minimizing vibration and keeping the noise in the laboratory at a comfortable level. The vacuum chambers are completely isolated from all form of lubricants and hermetically sealed even when major power failures occur.

Environment. Recent analyses revealed that the wavelengths of the tunable lasers are quite temperature sensitive [22]. The new CHILI laboratory at the University of Chicago is therefore thermally stabilized and provides a low vibration, draft-free environment.

Conclusions: CHILI reflects many recent developments in instrument design. It will be applied to a multitude of cosmochemical problems as to the analysis of the most challenging samples from the Stardust mission and maybe allow, after all, dating of presolar dust.

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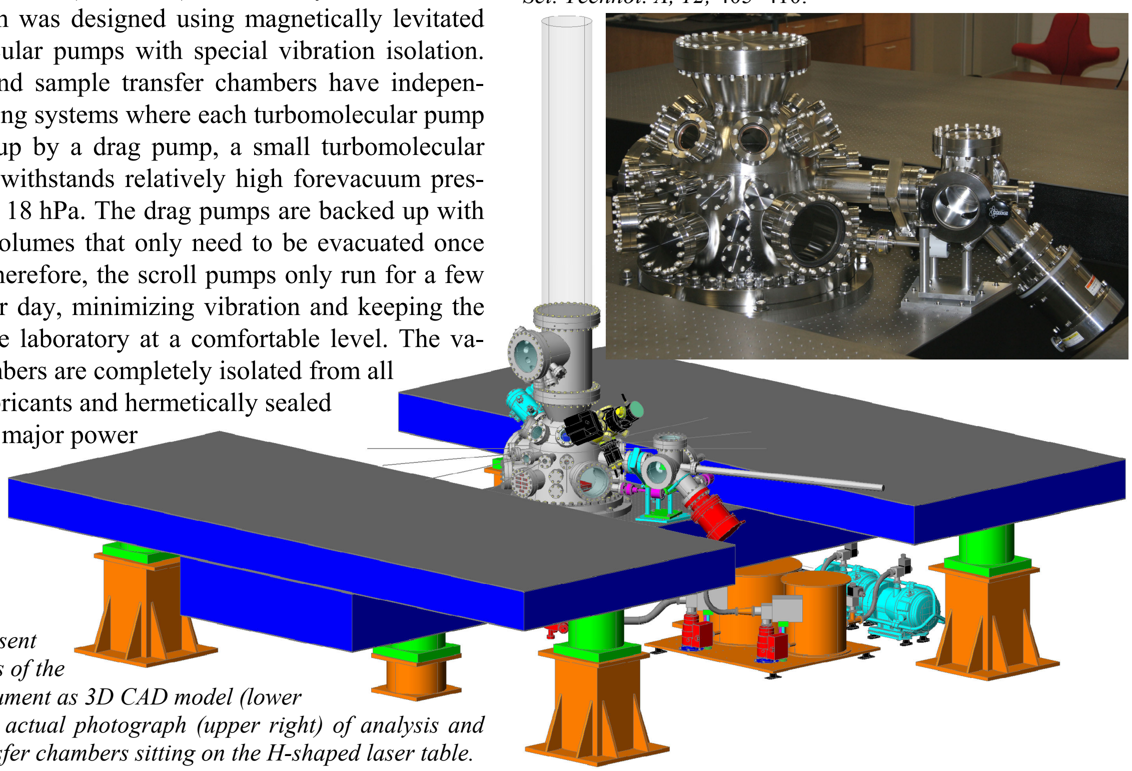

Figure. Present design status of the CHILI instrument as 3D CAD model (lower left) and an actual photograph (upper right) of analysis and sample transfer chambers sitting on the H-shaped laser table.