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Nuclear astrophysics with CHILI, the CHicago Instrument for Laser Ionization

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We recently completed CHILI, a laser resonance ionization mass spectrometer with an ultimate lateral resolution of 10 nm, a useful yield (atoms detected per atom removed from the sample) of 30–50%, and nearly complete suppression of interfering monatomic and molecular ions. CHILI is equipped with six tunable lasers, allowing simultaneous measurement of the isotopic compositions of three elements. We describe a series of measurements of presolar grains designed to constrain stellar nucleosynthesis models.

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1. Technical description

For the last five years, we have been designing and building CHILI (Chicago Instrument for Laser Ionization), a nanobeam RIMS (resonance ionization mass spectrometry) instrument (Figs. 1, 2) at the University of Chicago [1–7], which is poised to perform well beyond the capabilities of the current microbeam commercial SIMS instruments Cameca NanoSIMS, ims-7f, and ims-1280 and ANUtech SHRIMP II and Argonne National Laboratory's RIMS instruments CHARISMA [8,9] and SARISA [10].

The major technical advantages compared to earlier instruments are increased lateral resolution and useful yield, which should allow detection of 30–50 % of atoms of up to three elements simultaneously in volume elements (voxels) as small as 10^3 nm^3 (10×10×10 nm). For a typical mineral with a density of 3 g cm^{-3}, such a voxel contains ~10^5 atoms. To achieve these goals, a new design was necessary for CHILI, which has few parts in common with earlier instruments and which pushes technical specifications to their physical limits. Many of the

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components were designed and custom-built by us, including the vacuum chamber, bakeout system, ion optics, optical microscope, several power supplies and high voltage switching systems, tunable lasers, and transport optics, as well as all of the software to run the instrument. Below, we summarize the measures taken to achieve the goals of ultimate lateral resolution and sensitivity.

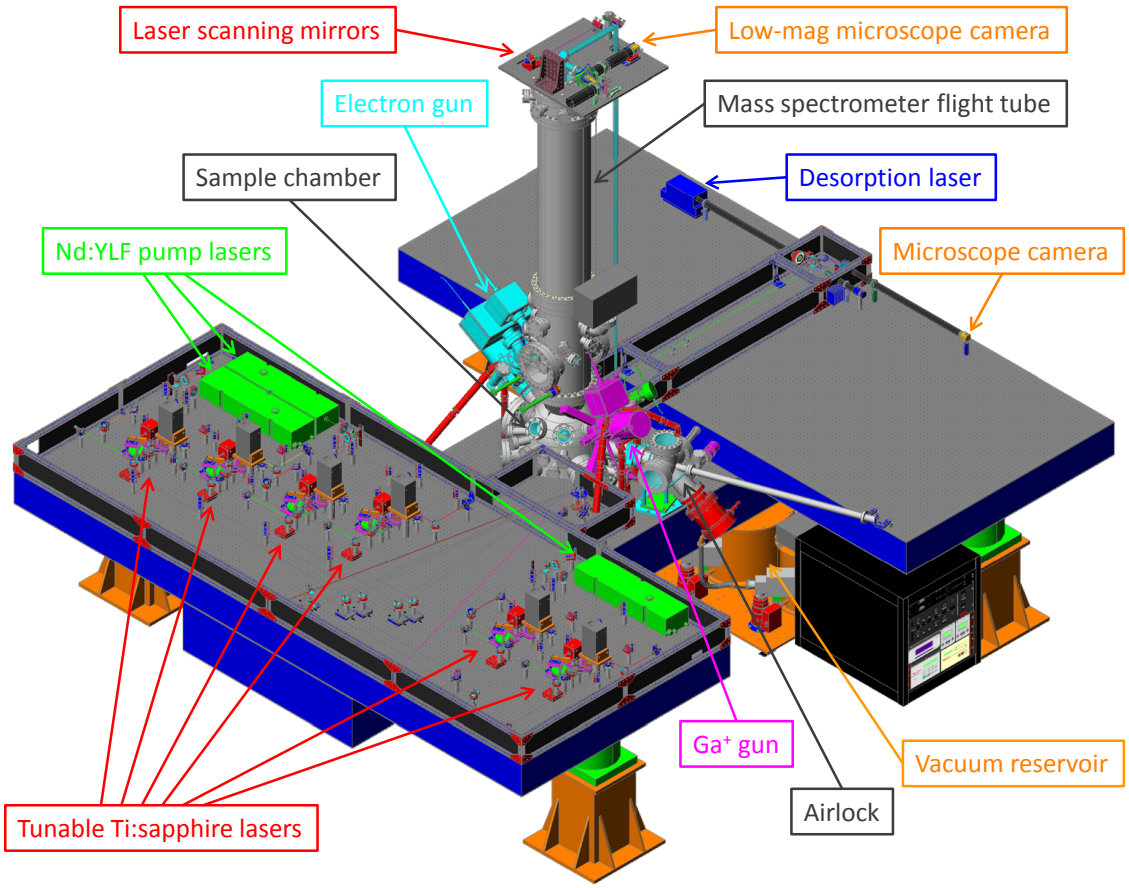

Figure 1. AutoCAD drawing of CHILI, showing major components.

A new home. A thermally stabilized, low-vibration, draft-free room with its own air handling system was specifically designed and built to house CHILI. A rigid extruded aluminum grid is attached to the ceiling and holds power supplies, high voltage switches, computers, etc., as well as a platform to work on the top of the mass spectrometer.

A sturdy base. All vibration-critical components, including turbomolecular pumps, analysis chamber, sample stage, ion and electron guns, mass spectrometer flight tube, and desorption and ionization lasers, are mounted on an H-shaped laser table, 4.27×3.66 m in size, that is supported by six active piezoelectric vibration cancellation legs. Great emphasis was placed on creating a rigid structure to minimize relative motion of the various parts and isolate them from possible sources of vibration.

Vacuum system. To further minimize noise and vibration, a vacuum system was designed that relies on magnetically levitated turbomolecular pumps with special vibration isolation and backed by drag pumps that withstand high fore-vacuum pressures. The drag pumps themselves

are backed by reservoirs that need to be evacuated with scroll pumps only once per month once the chamber is pumped down. The custom-designed vacuum chamber is completely isolated from all sources of lubricants. Internally mounted halogen lamps enable effective bake-out, allowing ultrahigh vacuum (UHV, $<10^{-9}$ hPa).

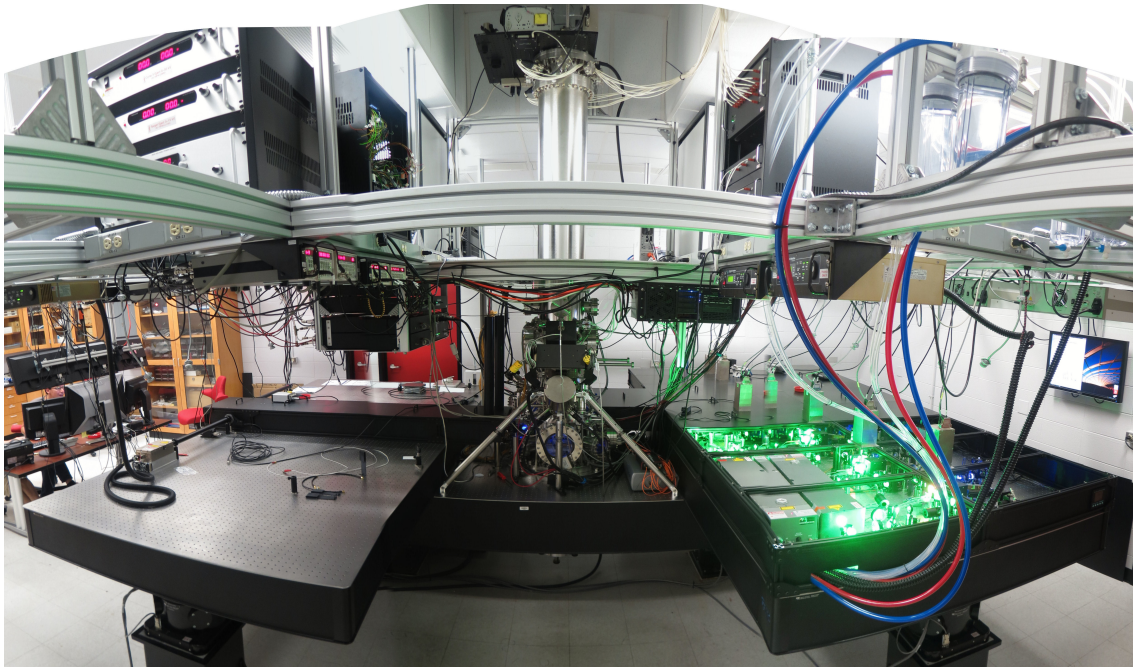

Figure 2. CHILI, viewed from the side facing the electron gun.

Holding and moving samples. Samples up to 45×65 mm in size can be mounted horizontally on an Alio Industries UHV-compatible, encoder-equipped, piezoelectric stage with sub-µm reproducibility. CHILI's removable sample holder is capable of mounting a variety of common types of samples, including 1-inch diameter polished sections, ½-inch, and 10-mm diameter SEM stubs, and TEM samples prepared by microtome or focused ion beam (FIB) techniques. Additional blank sample holders are available that can be machined to hold other types of mounts. Sample holders are loaded through an airlock, so it is not necessary to vent the instrument when changing samples. When inserted, the sample stage forms part of ~12 cm diameter flat disk that is an ion optical element.

Ion gun. For maximum lateral resolution in RIMS analyses, CHILI uses an Orsay Physics COBRA-FIB Ga liquid metal ion gun that can be focused to 2.5 nm. While such ion guns are mainly used for FIB applications, where they run with constant current, CHILI's time-of-flight mass spectrometer requires a pulsed ion beam. Since using the ion gun's existing beam blanking plates causes the ion beam to sweep across the sample each time the beam is blanked, a motionless blanking system was developed, in which a second pair of plates compensates for beam motion until the beam is completely blanked. This required design and construction of dedicated fast switching electronics. The ion gun has an accelerating voltage of 1–30 kV, allowing low voltage sputtering for fine-scale depth profiling. The maximum beam current (DC) is 50 nA, at which the beam spot is still ~1 µm in diameter. The ion gun will be used for desorbing from small spots and rastered areas (less than a few µm).

Scanning electron microscope (SEM). CHILI can operate as an SEM for sample imaging by using an Orsay Physics e⁻CLIPSE Plus field-emission electron gun, which can be focused to 4 nm, and an Orsay Physics secondary electron detector (SED) with minimal sensitivity to light. SEM imaging is important for locating small samples for analysis and for monitoring their gradual loss to sputtering or laser ablation during analysis.

Optical microscope. An optical microscope built in the Schwarzschild configuration is used for lower resolution, wide-field imaging. It uses spherical mirrors with holes in the center for passage of ion and light beams, not unlike a Cassegrain telescope. The light optical axis of the microscope is colinear with the ion optical axis for the secondary ions. Light passes from the sample, reflects off the mirrors, through the end of the mass spectrometer flight tube, bounces off two mirrors, goes down to the laser table and finally to a small high sensitivity CCD camera, for a total path length of 7 m. The resolution has been demonstrated to be <1 μm, near the diffraction limit. Part of the beam is diverted through a lens to a second CCD camera on a small optical table on top of the mass spectrometer flight tube to provide a low-magnification view.

Desorption laser. In addition, the optical microscope is also used to focus a UV desorption laser (Photonics Industries DC150-351 Nd:YLF laser; 351 nm, 1.5 W) onto the sample. Laser desorption is useful when a lateral resolution of ~1 μm is sufficient. The UV laser can deposit much more energy in a spot than the ion beam, allowing higher sample removal rates for minor and trace element analysis. A Nutfield Technology laser scan head allows the beam to be rastered. A blue guide laser is colinear with the desorption laser, so that the analysis spot can be seen through the optical microscope during desorption.

Laser ionization. Six tunable Ti:sapphire lasers have been built. They are pumped by three Photonics Industries DM40-527 (527 nm, 40 W) Nd:YLF lasers. The new laser systems have excellent power, bandwidth, and stability. In particular, the laser system takes advantage of our improved understanding about the bandwidths and stabilities required to provide precise isotopic ratios [11,12]. The Ti:sapphire lasers are tunable from ~700–1000 nm, but can be frequency-doubled (350–500 nm), tripled (233–333 nm), or quadrupled (205–250 nm) with nonlinear optical crystals. An important new feature of the laser system is a three-prism beam combiner that brings all six laser beams at different wavelengths into the analysis chamber on a single line. To use the photoionization laser light more effectively, the laser beams will pass eight times through the vacuum chamber using multiple reflections from a set of specially designed prisms. This will increase the size of the ionization volume by a factor of eight without sacrificing laser intensity. In single-pass instruments the beams would have to be defocused to cover the same volume and would therefore suffer a large loss in ionization efficiency. The laser port windows on the sample chamber, beam combiner, and multiple reflection prisms are all fixed at Brewster's angle to minimize reflective loss, achieving total system losses of <10% over very wide wavelength ranges. For most elements resonance ionization schemes require two tuned wavelengths, so three elements can be analyzed simultaneously.

Time-of-flight mass spectrometer. CHILI uses a reflectron-type time-of-flight mass spectrometer with a flight tube sitting vertically above the center of the laser table. The total height of CHILI is 3.45 m, including some light optical components sitting on top of the flight tube. The total length of the flight path for the photoions is ~3.6 m. The extraction field was optimized in order to make most effective use of the large ionization volume (6×6×3 mm).

Therefore, the acceleration voltage for the photoions is increased from 1–2 kV in previous instruments to 9 kV in CHILI. Increasing the accelerating voltage also increases the mass resolution and the efficiency of the detector. This represented a major design challenge for CHILI. Fast switching of such high voltages required liquid-cooled solid-state switches from Behlke Power Electronics GmbH. Currently, acceleration voltages up to 4 kV can be achieved, limited at the present time by the voltage we are able to apply to the reflectron, but will be increased to 9 kV in the future, once a redesigned reflectron is built and installed. Prior experience and extensive ion optical simulations using SIMION (from Scientific Instruments Services, Inc.) give us confidence that a useful yield of 30–50 % can ultimately be achieved. The use of SIMION was also important to optimize parameters for the reflectron that should allow for mass resolutions ($m/\Delta m$ at full-width half-maximum) above 3,000 at mass 100 u without any compromise in instrument transmission (which is >90 %). Even though selectivity is achieved via resonance ionization, high mass resolution and especially the attenuation of peak tailing significantly increases the abundance sensitivity and improves the overall performance of CHILI for low-abundance isotopes.

Detector and ion counting. CHILI is equipped with a Photonis Gen2 UltraFast microchannel plate detector with a pulse width of <300 ps (FWHM). This is matched with a FAST ComTec multiple-event time digitizer to achieve high data acquisition rates.

Software. All major subsystems of CHILI are controlled by our own software. Significant coding has been done to allow easy location of spots on images made with external instruments such as scanning electron and optical microscopes, and we are developing 3D imaging of isotopic and chemical composition as samples are sputtered or ablated away.

Initial testing. The first SIMS mass spectrum on CHILI was obtained in June 2014 and the RIMS mass spectra for Sr, Zr, and Ba were obtained in August 2014. The instrument is currently running standards in order to fully characterize the mass spectrometer and detector. Measurements on natural samples are anticipated by the end of 2014.

2. Nuclear astrophysics measurements with CHILI

Some of the planned measurements are of interest for nuclear astrophysics. In the order given, these measurements will require increasingly fine spatial resolution and high sensitivity as the full capabilities of CHILI are developed. (1) Simultaneous Sr, Zr, and Ba isotopic measurements of mainstream SiC grains will allow deeper understanding of observational constraints on the masses and internal ^{13}C distributions of ^{13}C pockets in AGB stars (e.g., [13–15]). (2) Simultaneous Cr, Fe, and Ni isotopic measurement of mainstream grains will probe the effects of galactic chemical evolution on the initial isotopic compositions of AGB stars. (3) Simultaneous Ti, Zr, and Mo isotopic measurements of carbide inclusions within presolar graphite will constrain timescales of grain formation around AGB stars and mixing in Type II supernova ejecta. (4) Mapping of primitive meteorites for Cr, Fe, Ni, Sr, Zr, Mo, and Ba isotopes might reveal new types of presolar grains, including those responsible for *r*-process enrichments seen in some progressive chemical leaching experiments on primitive meteorites and enrichments in the neutron-rich isotopes of the transition elements in some isotopically anomalous refractory inclusions in primitive meteorites.

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