FACILITIES FOR MÖSSBAUER AND LASER-INDUCED BREAKDOWN SPECTROSCOPY AT MOUNT HOLYOKE COLLEGE. M. D. Dyar[1], E. A. Breves[1], and E. C. Sklute[1]. [1], Dept. of Astronomy Mount Holyoke College, South Hadley, MA, 01075, USA, mdyar@mtholyoke.edu.

Introduction: The Mineral Spectroscopy Laboratory at Mount Holyoke College operates two different Investigator Facility Instruments that are available at cost to knowledgeable NASA-supported planetary program investigators. The Mössbauer spectroscopy laboratory, established in 1986, has supported both NASA and NSF research projects. The laser-induced breakdown spectroscopy (LIBS) laboratory was completed in 2015 and supports acquisition of LIBS data under Mars conditions. The goal of this abstract is to discuss the characteristics and availability of these facilities along with typical projects and uses.

Mössbauer Spectroscopy: The study of redox processes and their relation to the evolution of terrestrial bodies is of great interest to the planetary science community. Mössbauer spectroscopy remains the "gold standard" method for Fe^{3+}/Fe^{2+} determinations in powdered planetary materials such as meteorites, fulgurites, and individual mineral species used for spectral databases. Our Mössbauer spectroscopy facility has acquired roughly 1,800 spectra from 1986-1998, an additional >2,100 spectra from 1998-2000, and more than 6,300 spectra since 2000. *As such, a majority of geological Mössbauer papers published by U.S. researchers in the last decade has been based upon data acquired in our laboratory.*

Mössbauer spectroscopy differs from other types of spectroscopy in that a) the equipment runs continuously, and the lab must be maintained 365 days per year to optimize use of the expensive (~$10,000/year for 100 mCi) radioactive ^{57}Co sources, b) only a single sample can be run at a time, with data acquisition times of 4 hours up to 10 days, and c) fitting the data requires experience and involves highly-subjective curve-fitting, rather than end member-mixing. The result is that analyses are costly ($500/spectrum). These factors also make it inefficient and impractical for individual users to buy their own equipment. A steady stream of outside users has kept the lab in continuous operation for 30 years – we have never yet run out of samples in the queue to be run.

Our Web Research Co. (now See Co.) W100 spectrometer with a Janis closed cycle He cryostat, purchased in 1999, has capabilities that are fairly unique among Mössbauer labs in the U.S. Our use of a closed-cycle He cryostat makes it economical to acquire data at any temperature between 4.5K and room temperature. We routinely run samples with weights of 3-10 mg; for most materials, an optimal sample quantity is roughly 40 mg. The capability to run such small sample amounts makes it possible for us to study experimental run products, small samples that have been hand-picked from rocks and meteorites, and returned samples. Because we run randomly-oriented powders with controlled thicknesses, we avoid the orientation and thickness effects inherent in the milliprobe Mössbauer technique successfully implemented by Catherine McCammon [1].

We also correct all our data for Compton background, and use state-of-the-art models for spectral interpretation (including the Voigt-based implementation of the quadrupole splitting distribution and hyperfine field distribution techniques). With >35 years of experience in the field of Mössbauer spectroscopy of minerals, our research group has the personnel, the procedures, and the infrastructure to continue to the facilities to serve the planetary and terrestrial geologic community's needs well into the future.

Notable projects in support of NASA efforts have included many studies of mineral separates from meteorites including SNC's, ongoing work on lunar samples and eucrites, and many analyses in support of Ph.D. theses including work on fulgurites (Abigail Sheffer, ASU), synthetic pyroxenes (Rachel Klima, Brown University), space weathering (Sarah Noble, Brown University), acid weathering products (Nick Tosca, Stony Brook), and bioreduced minerals (Srishti Kashyap, University of Massachusetts) among many others. *More than 115 papers have been published in the past 10 years alone that make use of data from this laboratory.*

Finally, all data acquired in the Mineral Spectroscopy Laboratory at Mount Holyoke College are posted on a web site http://www.mtholyoke.edu/go/mars. *The web site is the largest on-line database of Mössbauer spectra of minerals anywhere in the world*. It provides an easily accessible data set of Mössbauer spectra of minerals collected over a range of temperatures. Data are posted in both graphical format (as JPG files) and as raw data in the form of ASCII text files. The web site also has an education link to provide information for those wishing to learn about how Mössbauer and other types of spectroscopy work. The site has received >720,000 hits since going live in 2005.

Laser-Induced Breakdown Spectroscopy (LIBS): There are currently four LIBS facilities available to U.S. users desiring data acquisition under Mars conditions: Mount Holyoke, Los Alamos, Johnson Space Center, and the University of Hawaii. There are numerous logistical difficulties associated with running samples at government laboratories because safety regulations make it impossible for visitors to run samples there by themselves. Furthermore, considerable effort is required to set up a LIBS system to mimic Mars data like those collected by the ChemCam instrument. The Mount Holyoke LIBS lab is set up to be operated by undergraduate students, and is thus accessible to outside users with limited training.

The Mount Holyoke LIBS instrument was designed to be analogous to the ChemCam flight instrument. It was designed and built in the LIBS User Facility at LANL. The instrument has three Ocean Optics HR2000+ user-configured spectrometers and a Quantel Ultra100 laser operating at 1064 nm, up to 15 mJ/pulse, 10 Hz, with a 6-ns pulse width. An attenuator is permanently integrated into the laser, allowing power density to be varied to obtain data that match those acquired on Mars (~2 GW/cm^2). A 12-inch cube vacuum chamber houses the sample tray (**Figure 1**). Samples are analyzed under a 7-Torr CO_2 atmosphere.

Standard protocol is to analyze every sample with the spectrometer exposure time set to 1 s, recording plasma emission for 10 laser shots. Five of these exposures are averaged for each sample spot probed, so each probed spot represents 50 laser shots. Five different spots on each pressed pellet are sampled to account for heterogeneity in our powdered samples, so there are 250 laser shots for each sample. Data are collected in UV, VIS, and VIS/near-IR wavelength ranges.

Standards: We have collected a reference database of >3500 geological standards with major and minor element analyses. Samples for this project were collected from a broad variety of sources. A majority of samples came from the x-ray fluorescence laboratory of J. Michael Rhodes at the nearby University of Massachusetts [2]. Pure minerals came from Dyar's collections. Rocks were contributed by Cal Barnes, Mark Brandriss, Marshall Chapman, Todd Feeley, Fred Frey, Mike Garcia, Wes Hildreth, Tony Irving, Barry Maynard, Alex McBirney, Scott McLennan, Damon Teagle, Dick Tollo, Peter Robinson, and Meg Thomson. Distribution of rock types is roughly 70% igneous, 25% sedimentary, and 5% metamorphic rocks. Minerals are largely common rock-forming silicates. Roughly 175 samples are doped with various chemicals including S, Ni, Cr, Mn, Co, and Zn [3]. All powders were pressed into pellets contained in 1 cm-diameter aluminum cups.

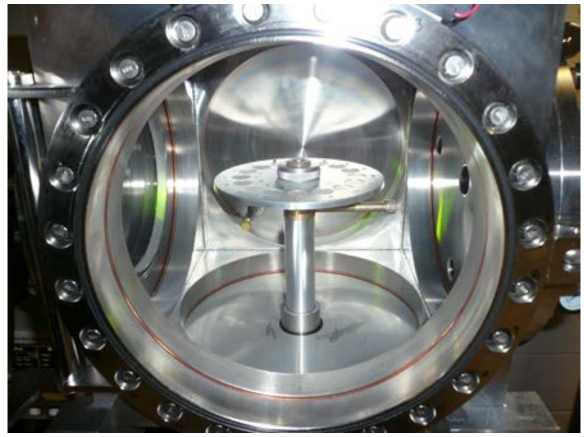

Figure 1. LIBS Mars chamber in the Mineral Spectroscopy Lab at Mount Holyoke College.

Data Pre-Processing: Software written for the LIBS lab matches the processing steps used on ChemCam [4], though each step has been tested and customized to produce optimal data. These involve a) subtracting a dark spectrum from the LIBS spectra to remove any fixed pattern noise or ambient baseline, b) recalibrating spectra onto a standard wavelength axis to account for spectrometer drift due to temperature changes, c) removing the Bremsstrahlung continuum to obtain a flat baseline, d) correcting for the known instrument response function, or gain, and e) correcting for geometry by dividing the photon count by the plasma area, collection solid angle, and spectral bin width. The MHC instrument uses LabView software for data acquisition and Matlab and Python routines for data reduction and analysis.

Tuning Instrument Parameters to Match Mars: Prior to acquiring data for use in calibrating Mars spectra, we carefully tuned our acquisition parameters to produce spectra that are a good match in intensity and spectral shape to those acquired on Mars.

Dissemination: We are in the process of building a web interface to allow outside user access to our spectra. We are committed to providing publicly-accessible calibration data for LIBS instruments in both planetary and extraterrestrial applications.

Conclusion: The Mineral Spectroscopy laboratory under Dyar's direction has maintained continuous operation since 1986. We have set a standard for high quality Mössbauer data and interpretations, and we expect to build upon that record of success with our new LIBS laboratory as well.

References: [1] McCammon C. (1994) *Hyperfine Interact., 112*, 269-273. [2] Rhodes J. M. et al. (1996) *JGR, 101*, 11729-11746. [3] Breves, E. A. et al. (2015) *LPS LXXVI*, Abstract #2339. [4] Wiens R. C. et al. (2013) *Spectroch. Acta B*, B82, 1-27.