BUILDING ANALYTICAL COMPETENCE FOR GEOSCIENCE STUDENTS THROUGH USE OF RAMAN SPECTROSCOPY. J. B. Brady[1], M. D. Dyar[2], E. McGowan[3], and P. Bartholomew[4], [1]Dept. of Geology, Smith College, Northampton, MA 01063 jbrady@smith.edu, [2]Dept. of Astronomy, Mount Holyoke College, South Hadley, MA 01075 mdyar@mtholyoke.edu, [3]Math, Physics, and Computer Science, Springfield College, Springfield MA 01109, emcgowan@springfieldcollege.edu, [4]Dept. of Biology and Environmental Sci., University of New Haven, West Haven, CT 06516, PBartholomew@newhaven.edu.

Introduction: Traditionally, a geologist's analytical toolkit consisted of a hand lens, rock hammer, acid bottle, magnet, and perhaps a polarizing light microscope back in the laboratory. In geoscience professions, these tools are increasingly being supplemented by field and laboratory instrumentation that utilizes spectroscopy. The availability of newly-developed, lower-priced spectroscopic instrumentation and the attention of geoscientists to problems (e.g. nanogeoscience, biomineralogy, mineral physics) that cannot be addressed by classical mineralogical techniques are requiring a shift in the skill sets needed by our students. Effective use of spectroscopic tools can pose problems for geosciences students in an era when chemistry courses are disappearing from geology/earth science/environmental science major requirements at institutions already stretched thin to cover the breadth of the geosciences alone. To analyze critically the data collected, students must become conversant in the language of chemistry and the fundamental characteristics of atoms that inform various spectroscopic methods. Learning outcomes for geoscience departments are increasingly articulating this need for analytical competence. We report here results of a project promoting analytical competence in introductory and mineralogy classes in geology curricula through use of spectroscopic tools including Raman spectroscopy.

Project Background: With support from the Division of Undergraduate Education at the National Science Foundation, we purchased two portable B&WTek i-Raman® Plus spectrometers to be shared among our institutions. Each system has a 532 nm laser and a TE-cooled CCD detector, and covers a Raman shift range of 175-3300 cm^{-1} with a center resolution of ~3.0 cm^{-1} at 614 nm. We also purchased trigger-enabled probes for each instrument, as well as a microscope adapter compatible with our Olympus polarized light microscopes. We purchased B&WTek's material identification software, knowing that minerals were only sparsely represented therein, with plans to create our own calibration database.

We downloaded a set of the unoriented and processed Raman spectra included on the RRUFF database [1] as ascii files, and converted those files to BWTek-readable format. In addition, we are collecting test spectra from known samples in our own mineral collections to add to our Raman mineral library. We are in the process of creating learning modules based on the following themes:

Name That Mineral asks the introductory students to identify samples from a group of common rock-forming minerals using Raman and FTIR.

What's That White Powder? asks students to become forensic scientists and identify the mineralogy of common white substances, including baby powder, blackboard chalk, rock-climbing chalk, and wallboard.

Gemstones: Let the Buyer Beware lets student use both Raman and FTIR to compare the spectra of naturally-occurring vs. treated gemstones, becoming familiar with the effects and associated spectral signatures of the various treatments.

Mineral Synthesis and Breakdown helps students develop the concept that minerals can be both the products and reactants for chemical reactions, and that these are chemically linked. Students will learn to design, execute, and evaluate synthesis and/or decomposition experiments using Raman and FTIR.

Twist and Turn: The Geometry of Molecules in Minerals is a series of experiments on minerals from which students will collect Raman spectra in various crystallographic orientations. Optical characteristics of several minerals in the same array of orientations will be examined, providing the opportunity for students to synthesize concepts about the interaction of visible light and laser light with lattices, the geometry of molecular groups within lattices, and the information derivable from multiple analytical techniques.

Pottery and Glazes: Before and After Firing will examine the minerals used in pottery and in glazes and the changes they undergo during the firing process. This experience can then be applied to the study of pottery from various sources, as used by art historians and archeologists.

We expect these modules to be available for distribution by the fall semester of 2015. Until then, we are working on addressing the issues that have arisen for practical classroom use of Raman spectroscopy, as given in the following list.

Lesson Learned #1: Safety Protocols Required for Classroom Usage. The process of gaining approval for safe operation of Class IIIb laser Raman instruments in a large class/laboratory setting was time-

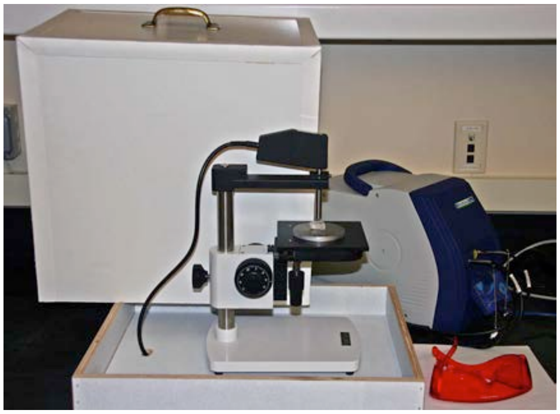
Figure 1. Home-made enclosure for B&WTek i-Raman Plus, used for safe operation of the instrument in classroom settings.

consuming. In general, our institutions required the following procedures for usage. When the instrument is operated, all students in the room must wear laser safety goggles. Given the visual impairment and cost of the goggles, this requires that the Raman be located in a different room than the entire lab section. Moreover, to help prevent accidental viewing of the laser beam during each experiment and to exclude room light, we built an enclosure from plywood and foam core board to contain the fiber-optic probe and sample holder (Figure 1). Our safety protocol requires that the enclosure be closed during Raman data collection. After a training session, students are permitted to operate the Raman spectrometer without supervision.

Lesson Learned #2: Effects of Optical Density. While there are variations in Raman intensity that are driven by structure and chemistry, it can also be generalized that dark and opaque minerals produce less Raman signal because the laser does not penetrate as deeply as in more transparent materials, and thus samples less mineral. It is difficult (but important!) for students to understand parameters such as sampling depth and signal to noise ratios, but some guidance is needed to help obtain useful spectra for minerals. Thus, we are developing different procedures for use on materials with varying optical densities. These include default acquisition times for transparent vs. dark minerals.

Lesson Learned #3: Photoluminescent Interference (PL). PL interference in Raman spectra can reduce S/N ratio by greatly elevating background, introduce non-Raman peaks (e.g., PL from REE centers) and/or completely overwhelm any Raman signal. Attempts at mineral identification from spectra containing PL interference will produce reduced search/match scores or entirely erroneous results. Introductory level students will only become frustrated with identification software that does not appear to be working unless they can be taught to recognize PL interference.

We have reviewed examples of 532nm RRUFF spectra that exhibit various amounts and spectral shapes of PL interference in the region of interest for mineral identification (100-1500cm^{-1}). We plan to develop a module about "recognizing and understanding fluorescence and photoluminescence in minerals" including examples of from the RRUFF database to help students understand this issue. This will both improve students' success with applying Raman spectroscopy to mineral identification and deepen their understanding of atomic and lattice responses to light.

Lesson Learned #4: Mineral Databases. Several issues have arisen for this project regarding mineral databases. BWTek sells a mineral database, but it is expensive, does not contain many minerals, and its format is proprietary. With assistance from B&WTek, we have converted the RRUFF database into their format so it can be used with their search/match software. It turns out that the RRUFF database is so comprehensive that it contains many rare minerals that students are unlikely to encounter in undergraduate coursework. Thus, we are finding it necessary to create multiple smaller databases for use in the introductory and mineralogy classes. With fewer choices, students have a higher success rate and a more positive experience. We have not yet found a good open source database for non-mineral inorganic materials.

Lesson Learned #5: Mineral Mixtures. To date, there is no simple way to deconvolute Raman spectra containing mixtures of minerals in a fine-grained sample (e.g., basalt). Work is in progress [2] to use sophisticated machine learning techniques for this purpose, but those are unlikely to be practical for use in undergraduate teaching applications. Thus, use of the Raman system on fine-grained materials in hand sample causes difficulties in interpretation of spectral results. Students get the best results when a single mineral can be easily centered in the laser beam.

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