



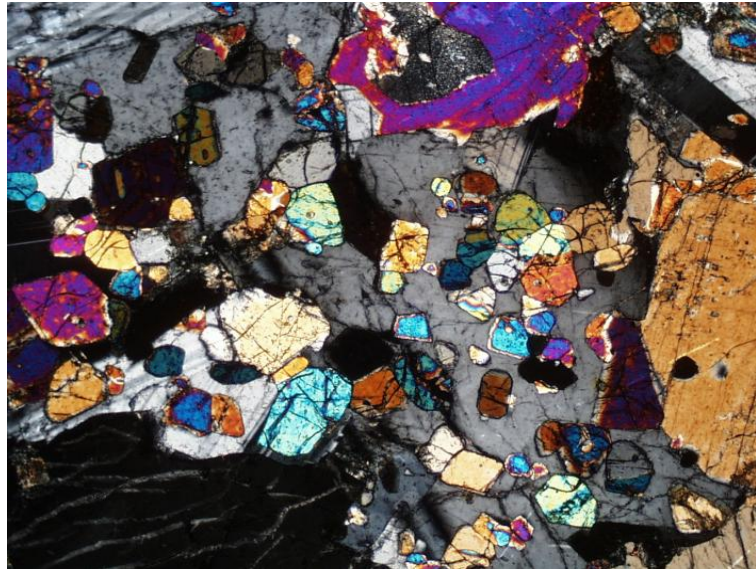
## Micro-Raman Spectroscopy in Thin Section Analysis of Rock Mineralogy

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### Introduction

Correct identification of mineral phases in rock thin sections (Figure 1) is essential to petrographic and petrologic analysis of rocks.

Traditionally, analysis using polarized transmitted light and reflected light microscopy have been the standard techniques employed, with optical cathode-luminescence microscopy used to a much more limited extent. Optical microscopy techniques are taught in core courses in all undergraduate geology curriculums and petrographic microscopes are part of the basic instrumentation of all academic geology departments, most State and Federal geology agencies (e.g. U.S. Geological Survey), and many private geoscience companies in the mineral and energy resources sector.



**Figure 1.** Photomicrograph of a rock thin section showing a variety of silicate mineral phases in cross-polarized light.

Successful identification of most mineral phases using a variety of standard optical characteristics visible under low to moderately high-resolution (20x-1000x) is fairly routine. However, as the sizes of mineral phases decrease to the sub 100-micron level standard optical techniques become much less successful. Additionally, many common minerals are solid solutions chemically and identification of the various members of a series is either much more difficult or simply not possible using optical techniques alone. To overcome the limitations of simple optical examination, geologists have resorted to a variety of very high-resolution techniques providing chemical as well as optical information over the past 5-6 decades. These include scanning electron microscopes with energy dispersive spectrometers (SEM-EDS), electron microprobes (EMP) and Raman microscopes (RM). While SEMs and EMPs, provide both very high-resolution imagery (sub-micron scale) and mineral phase chemistry (micron scale) their acquisition costs range from hundreds of thousands to over a million dollars, annual maintenance costs of thousands to over ten thousand dollars, dedicated climate-controlled lab space, and usually a salaried technician. Micro-Raman spectroscopy offers a modest acquisition cost of several tens of thousands of dollars not including a petrographic microscope, no manufacturer maintenance contracts, no dedicated climate-controlled lab space, and no specialized technicians. Commercial thin section preparation costs are also modest (\$20-\$ 40 per section) and many geology departments already have facilities able prepare thin sections in-house.



### Micro-Raman System

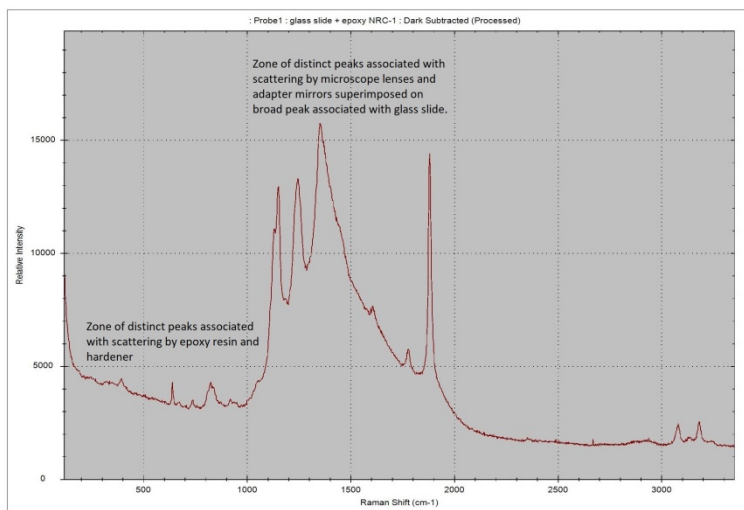
The examples provided below exhibit the application of micro-Raman spectroscopy to mineral identification in polished rock thin sections using a B&W Tek i-Raman® Plus portable Raman system (785 nm laser excitation and spectrometer with BWSpec® and BWID® software) interfaced with an Olympus BX-40 microscope equipped with an X-Y mechanical stage and 10x, 50x, and 150x metallurgical objectives (Figure 2). The 785 nm laser provides the greatest flexibility for mineral analysis in terms of excitation energy, fluorescence, and light absorption/heating.



**Figure 2.** Photograph of the B&W Tek i-Raman Plus Raman system (left) interfaced with an Olympus polarizing microscope (center) as described in the text. Desk is 48 inches wide.

### Mineral Identification in Rock Thin Section Using Micro-Raman Spectroscopy

Micro-Raman mineral analysis offers several important enhancements to standard optical techniques (Nasdala and others, 2004). First, based on the diameter of the excitation beam and the specifications of microscope objective lens, illuminated spot sizes of single digit to several tens of microns can be attained. This results in the ability to generate spectra from very-fine grain sizes, sizes that are difficult to impossible to acquire standard interference figures for birefringent minerals. Because many



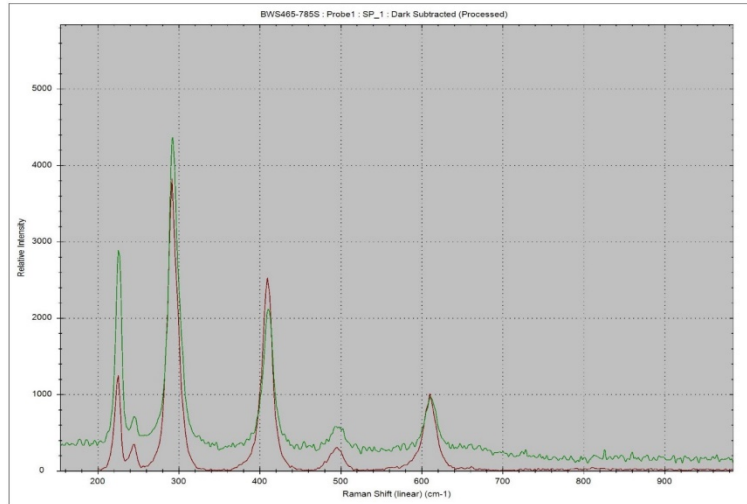
**Figure 3.** Acquired spectrum of standard glass microscope slide coated with epoxy

accessory and secondary alteration minerals occur in very fine grain sizes, this greatly improves the ability to identify minerals in their in-situ textural context with other minerals in the rock. Secondly, micro-Raman analysis can provide chemical identification and semi-quantitative chemical information on many solid-solution minerals as well as distinguishing polymorph phases of the same chemical composition. Finally, micro-Raman spectroscopy offers the ability to switch seamlessly between optical and Raman analysis simply by turning off the microscope light source during laser illumination\*.



While polished (no cover-slip) thin sections provide the best conditions for Raman analysis, covered thin sections also can be used. In both cases, because the rock specimen is mounted on a glass microscope slide using an organic epoxy resin (plus hardener), all acquired Raman spectra will include the scattering signal of the slide and bonding agents as well as that resulting from the passage of the laser beam through microscope objectives and adapter mirrors. Fortunately, the dominant signal of these materials is fairly easily recognized and therefore, can be distinguished from diagnostic mineral peaks when making mineral identifications (Figure 3).

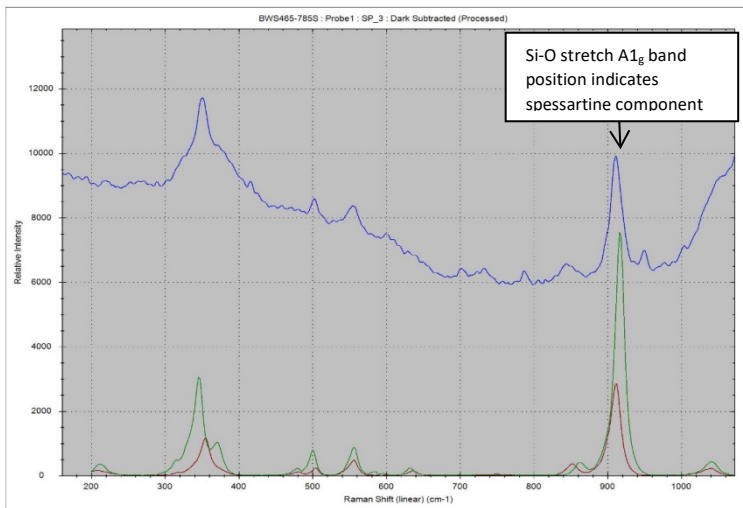
**\*This application note will only address mineral identification in thin section using standard widefield microscopy, not confocal laser scanning. All 'acquired spectra' from ~16 micron excitation spot diameters.**



**Figure 4.** Acquired spectrum (green) of unknown opaque grain in polished section compared to University of Arizona RRUFF reference spectrum of hematite (brown) (100% laser power; 2 second integration time for acquired spectrum).

## Examples

Optical identification of opaque minerals in thin section is highly limited without reflected light



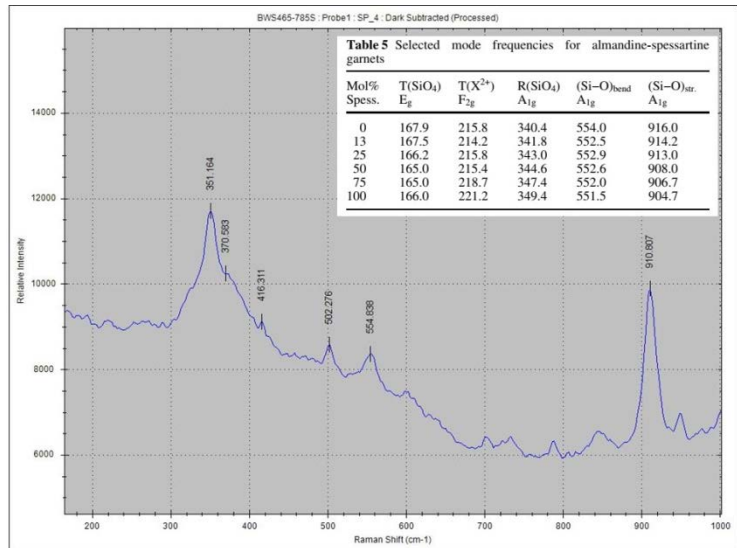
**Figure 5a.** Acquired garnet spectrum (blue) plotted with RRUFF reference spectra of almandine garnet (green) and spessartine garnet (brown). Acquired garnet spectrum shows an intermediate composition in the almandine-spessartine solid solution series. 100% laser power, 10 second integration time for acquired spectrum.

capabilities, and even with this capability is often difficult. Micro-Raman analysis using a standard transmitted light petrographic microscope, however, can provide clear identification of common opaque mineral phases (Fe-, Fe-Ti, Fe-Cr and Mn-oxides, graphite, and all sulfides) provided correct excitation conditions are employed (low power densities to lessen local heating/alteration artifacts (Nasdala and others, 2004). Figure 4 illustrates the comparison of an acquired hematite spectrum with a reference hematite spectrum. The agreement of the Raman peak positions and relative intensities between the collected spectrum and library hematite spectrum indicates the sample is hematite.

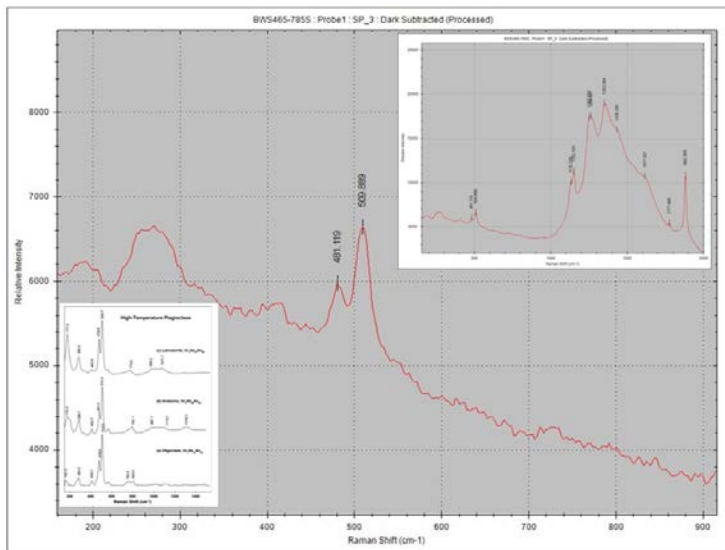




Garnet, a common metamorphic mineral occurs in several isomorphous solid-solution series, the Ca-Fe/Ti-Cr garnet series and the (Mg-Fe-Mn) series. Micro-Raman analysis can provide valuable semi-quantitative chemical information about members of these series (Kolesov and Geiger, 1998). The spectrum in Figure 5 illustrates how variations in major Raman peak position can be used to estimate ranges of mole percent MnO/FeO in the spessartine-almandine garnet series. The primary  $A_{1g}$  peak around  $900\text{ cm}^{-1}$  indicates a mole percent spessartine component in the 25-50% range.



**Figure 5b.** Same acquired garnet spectrum as in 5a showing main Raman peaks and Table 5 of Kolesov and Geiger (1998) illustrating ranges of mole % spessartine component in almandine-spessartine solid solution.



**Figure 6.** Acquired spectrum (red) of plagioclase feldspar from Marcy Anorthosite massif, northern NY.

Upper right insert shows extended spectrum (to  $2000\text{ cm}^{-1}$ ) including strong glass slide + epoxy luminescence signature in the  $1100\text{--}1900\text{ cm}^{-1}$  Raman shift range. Lower left insert showing spectra for oligoclase, andesine, and labradorite plagioclases as determined by Freeman and others (2008). 100% laser power, 10 second integration time for acquired spectrum.

The insert in the upper right of Figure 6 illustrates the complete acquired spectrum and how the strong luminescence generated by the glass slide and epoxy (see Figure 3) does not interfere with the diagnostic portion of the mineral spectrum. Note also that the broad, rounded peak from approximately  $240\text{--}280\text{ cm}^{-1}$  is most likely also a luminescence artefact caused by the well-known concentration of Europium in calcic plagioclase.

Plagioclase feldspar ( $\text{NaAlSi}_3\text{O}_8\text{--CaAl}_2\text{Si}_2\text{O}_8$ ) the most common silicate solid-solution mineral, occurs in a wide range of igneous, metamorphic, and sedimentary rocks. The six named members of the plagioclase series (albite, oligoclase, andesine, labradorite, bytownite, anorthite) are an essential criterion used in most igneous rock classification schemes. While there are several optical methods that are available to identify series members (refractive index, extinction angle of albite twins), these are commonly difficult to obtain with suitable precision. The acquired spectrum in Figure 6 is from a plagioclase feldspar grain in a coarse-grained igneous rock. The two fairly narrow peaks at approximately  $481$  and  $510\text{ cm}^{-1}$  are diagnostic of andesine plagioclase as determined by Freeman and others (2008) and depicted in the insert to the



## Conclusions

Identification of mineral phases in rock thin section is sometimes difficult to impossible using traditional optical techniques alone, especially for very fine-grain sizes (< 100 microns), common solid-solution series members (e.g. plagioclase, garnet, pyroxene series members), and opaque minerals. Micro-Raman imaging using an interfaced laser/spectrometer system such as the B&W Tek i-Raman Plus system with a standard petrographic microscope with 100x-150x objective lenses (e.g. Olympus BX 40 and 50 series) can overcome these optical identification issues while allowing the microscope platform to be used for traditional petrographic analysis as well. Micro-Raman analysis also can provide valuable semi-quantitative chemical information about mineral phases. Given the relatively modest acquisition costs, almost zero annual maintenance costs, and lack of dedicated operational technician and special lab space requirements, micro-Raman systems represent a very attractive technology enhancement for all College and University geoscience departments, as well as government geoscience agencies, and private mineral resource consulting firms.

## References Cited

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