

RAMAN SPECTROSCOPY AND MICRO-SPECTROSCOPY OF FELDSPAR



APPLICATION NOTE RAMAN-021 (A4)

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Abstract

This application note documents the use of a TSI ChemLogix™ ProRaman-L instrument with and without a microscope to examine feldspar mineral samples.

Motivation

Feldspars ($KAlSi_3O_8$ – $NaAlSi_3O_8$ – $CaAl_2Si_2O_8$) are a group of rock-forming tectosilicate minerals that make up nearly half of the Earth's continental crust by weight. Feldspars crystallize from magma as veins in igneous rocks and are also present in many types of metamorphic rock. "Plagioclase" is the name of a group of feldspar minerals that form a solid solution series ranging from pure albite, $Na(AlSi_3O_8)$, to pure anorthite, $Ca(Al_2Si_2O_8)$. Minerals in this series are a homogenous mixture of albite and anorthite. The names of the minerals in the series are arbitrarily given based upon their relative abundance of albite and anorthite. The minerals of the plagioclase series are shown in Figure 1 along with their relative abundance of albite and anorthite.

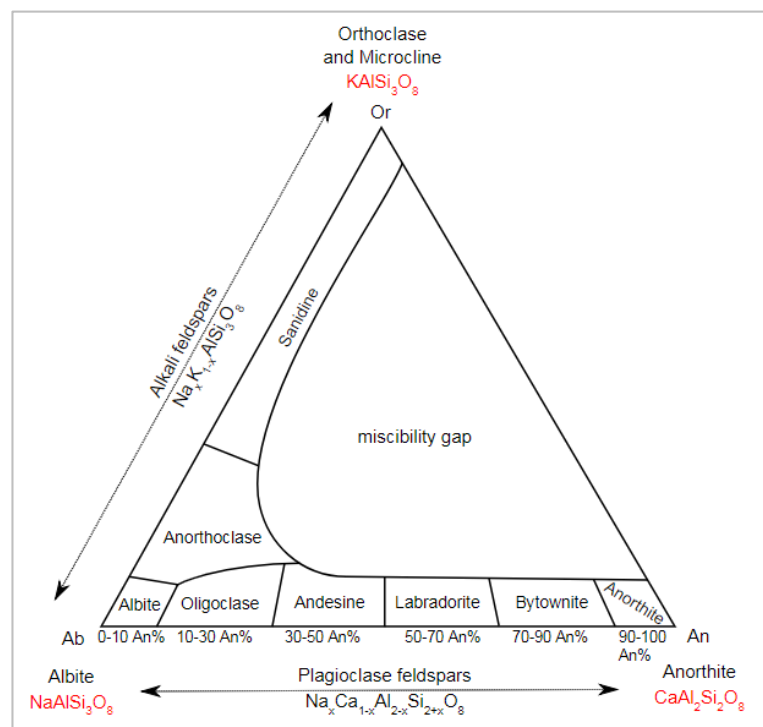


Figure 1. Compositional phase diagram of the feldspar solid solutions.¹

Members of the plagioclase group are the most common rock-forming minerals. They are important to dominant minerals in most igneous rocks of the Earth's crust. They are major constituents in a wide range of igneous rocks including granite and basalt, among others. Plagioclase minerals are important constituents of many metamorphic rocks, such as gneiss, where they can be inherited from an igneous protolith or formed during the regional metamorphism of sedimentary rocks.

Feldspar identification is of interest to geologists who endeavor to understand the evolution of the Earth's surface, but also is interesting to the planetary science community. Feldspars are one of the main minerals in Martian meteorites and plagioclase is the most abundant mineral on the Moon.^[2]

Samples

The samples were two rocks with cut faces, each about 1" long and 0.4" deep and wide. One of the rocks is a grey material with very small white specks, barely visible to the naked eye. The other is a white mineral with black veins running through it. These rocks were cut with a microtome and mounted on microscope slides.

Measurements and Results

The larger rock samples were analyzed using a TSI ChemLogix ProRaman-L unit with a wide spectral range (100-3300 cm^{-1}). Laser excitation was performed at 785 nm with 85 mW.

Measurement on these samples was performed by mounting the measurement probe in a ring stand and presenting the rock samples on the lab bench top, because the samples were too big to put in the xyz translation stage normally used to present samples to the laser. A high numerical aperture lens assembly was used with an approximate spot diameter of 65 μm . Room light was blocked from the measurement region with a plasticized black cloth laser curtain.

Microscope slide sections were analyzed with the ProRaman-L interfaced with an Olympus CX31 microscope. The spot diameter at 40x is about 25 μm . Approximately 10 mW of excitation power was used to collect spectra at a variety of locations.

The white and black sample had regions large enough to attempt differentiation of the materials related to the colors separately, even without a microscope. Background corrected data of both regions is shown plotted against samples of albite and anorthite, at opposite ends of the feldspar solid solution diagram, from the RRUFF database^[3] in Figure 3, matched with SpectraGryph.^[4] This spectrum shows that even though it appears by eye that the excitation laser is only positioned on the black portion of the rock, there is still a mixture of compositions in the excitation region.

Because of the relatively homogenous appearance of the gray rock, we submitted this sample to interrogation with the laser without selecting any given location. The resultant spectrum gave indication of at least three different materials present in the spot of the excitation laser.



Figure 2. Feldspar rock samples, raw and prepared on microscope slides.

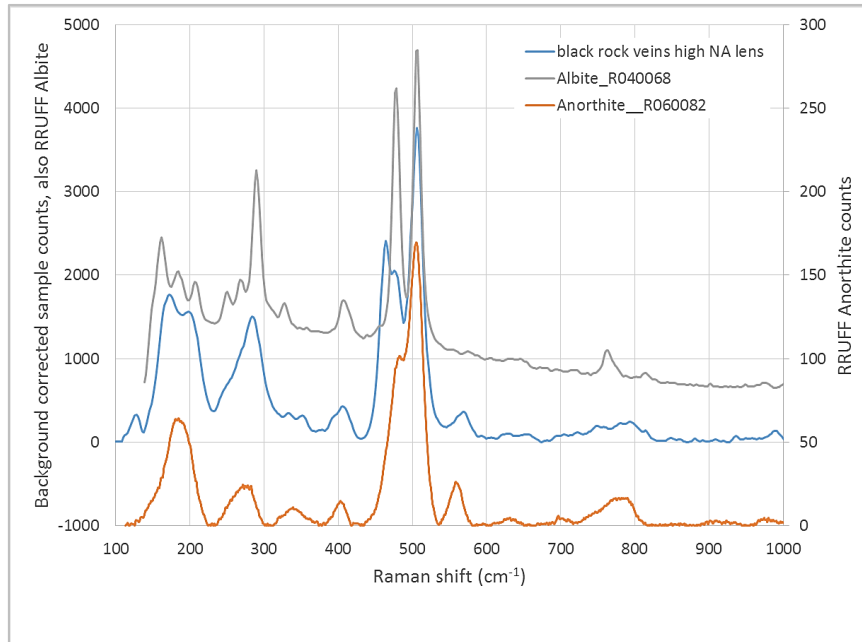


Figure 3. Raman spectrum of black material plotted with albite and anorthite spectra from the RRUFF database. Spot size for this data is about 60 μm in diameter.

Both these results, overlapping spectra of multiple minerals present in the interrogated region, suggest the use of a microscope, both to select the region for analysis and to reduce the interrogation spot size. The microscope, used at 40x, permits the user to more precisely choose the analytical target and the smaller spot size increases the likelihood that a single material in a complex matrix will be observed with the laser.

The samples used on the microscope were the slide-mounted microtome rock sheets. The spectra of these samples contain silica features associated with the slide itself, but the mineral features are clear in the spectral region below them.

The Raman spectra collected on the feldspar minerals with the high numerical aperture lens assembly area can be used to identify the component materials. However, in both samples, on the scale of the regular Raman analysis (i.e. with no microscope), there are multiple minerals present in the interrogation spot. The background corrected spectra were compared against RRUFF database^[3] entries to establish the ID of the dominant material. The IDs provided by SpectraGryph^[4] were generally in the 0.6-0.8 range, lowered by the presence of spectral features from multiple compounds.

As is clear from Figure 3 and 4, normal scale Raman spectroscopy provides averaged composition information when used on samples that have feature sizes smaller than the laser spot size. Figure 3 shows the spectrum collected from the black veins in the white and black rock (blue trace) compared with the end-member feldspars. The spectrum of the black vein is largely composed of albite, but has a contribution from quartz at 464 cm^{-1} . Figure 4 is more complicated. The background corrected spectrum of the gray rock (blue trace) is clearly a mixture of graphitic carbon materials and albite, with a small contribution of quartz. A few extra spectral features remain unassigned.

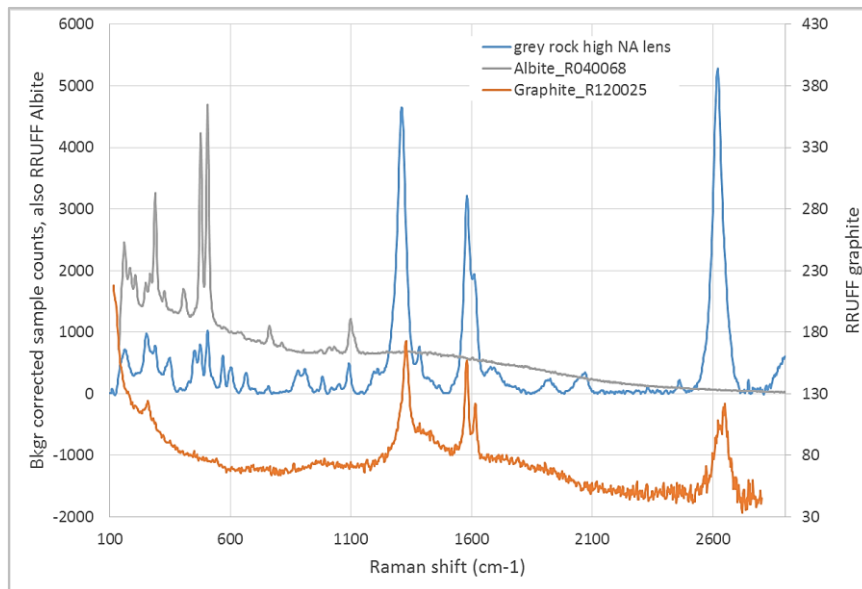


Figure 4. Raman spectrum of gray sample plotted with albite and graphite spectra from the RRUFF database. Laser spot size for this data is about 60 μm in diameter.

When the use of the microscope is invoked, individual compounds are easier to identify, both by eye and by computer-aided matching. Additionally, the microscope reveals that far from being a homogenous material, the grayish rock is quite heterogeneous, not surprising based upon the observed spectra. A photograph of the microtome sample of the gray stone using a 10x objective is shown in Figure 5.

The spectrum of one of the white regions in the photograph is shown in Figure 6. At the smaller spatial resolution, at this location, the white material reveals itself to be pure quartz. The features in the black and white sample are not quite as well differentiated, but the use of the microscope simplifies the spectrum dramatically, leaving only feldspar signals, for the most part.

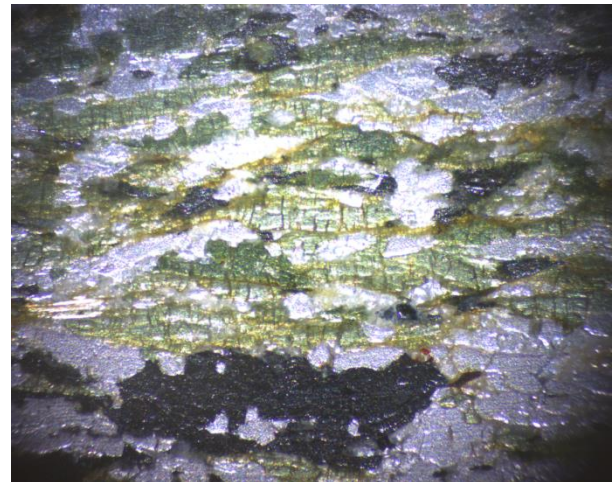


Figure 5. Photograph of slide of gray rock, 10x through microscope.

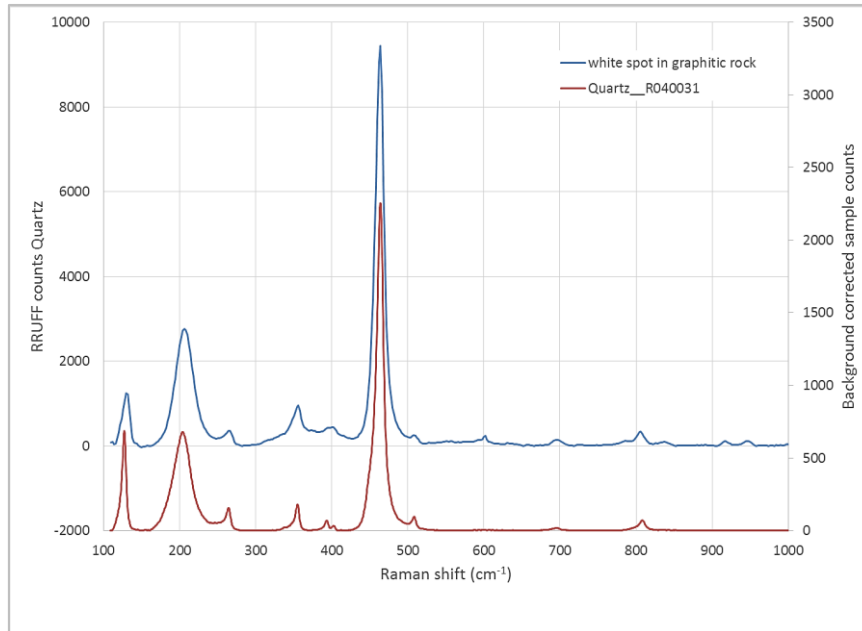


Figure 6. Micro-Raman spectrum of a white region in the gray rock. Features from slide preparation have been cropped out.

The spectrum in Figure 7 matches well to both RUFF spectra shown, but better to the oligoclase, in this case matching the relative peak heights of the 480 and 505 cm^{-1} features in that material. These so-called “Group I features” described in Freeman et al [2] as peak position of the strongest Raman band of many tectosilicates shows an inverse correlation with the size of the ring made by the T04 oxide tetrahedral geometry. These authors state that this strongest peak in the Raman spectrum of many tectosilicates can be used to identify the specific type.

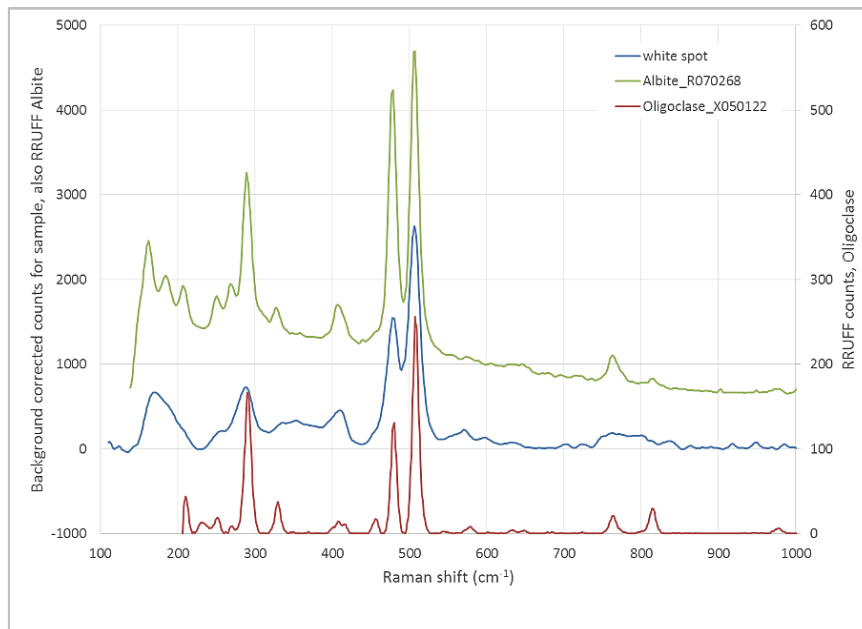


Figure 7. Micro-Raman spectrum of a white region in the black and white rock. Features from slide preparation have been cropped out.

Summary

This application note has focused on the ability of the smaller spot size in the microscope system to analyze regions of smaller feature size and to acquire spectra of purer materials in complex matrices. It also illustrates how Raman spectroscopy can be used to identify feldspar materials, useful on this planet and others.

References

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2. Freeman, J.J., A. Wang, K.E. Kuebler, B.L. Jolliff and L.A. Haskin, "Characterization of Natural Feldspars by Raman spectroscopy for future planetary exploration," *Can. Mineralogist*, **46**, 1477 (2008).
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4. F. Menges "Spectragryph - optical spectroscopy software", Version 1.2.4, 2016-2017
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