

Remote Raman Detection of Natural Rocks

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Introduction

Standoff remote Raman technique is increasingly highlighted as a viable method for planetary surface chemical analysis. This technique requires no sample preparation, transfers minimal to no damage to the targeted sample, and can be used under daylight conditions; saving time and increasing the number of accessible targets. The University of Hawaii (UH) in collaboration with Los Alamos National Laboratory (LANL) and NASA Langley Research Center, has developed a Compact Remote Raman+LIBS+Fluorescence System (CRRFLS) that is capable of Raman, LIBS, and fluorescence measurements under daytime conditions from standoff distances. The instrument is shown in Figure 1. This work is in support of the Mars 2020 mission where UH is collaborating with LANL and French partners IRAP and CNES, to develop the SuperCam instrument that will be a part of the Mars 2020 rover. The instrument will perform remote chemical analysis of Mars surface rocks using Raman, LIBS, and time-resolved fluorescence spectroscopy. [1]

In the past we have demonstrated remote Raman detection capability for a variety of minerals. The CRRFLS has been able to successfully acquire high quality Raman spectra of various light and dark minerals, water, water-ice, CO₂ ice, organics, and inorganic chemicals at distances of up to 50 meters with a 10 sec integration time [2-6]. Here, we extend our detection capability to investigate natural rocks using remote Raman spectroscopy.

Several igneous and metamorphic rocks were surveyed using the CRRFLS to identify the mineral constituents for the rocks. The following results display the ability of a portable compact remote Raman+LIBS+Fluorescence system for detecting various mineral phases, in natural rocks from a distance of 5 meters.

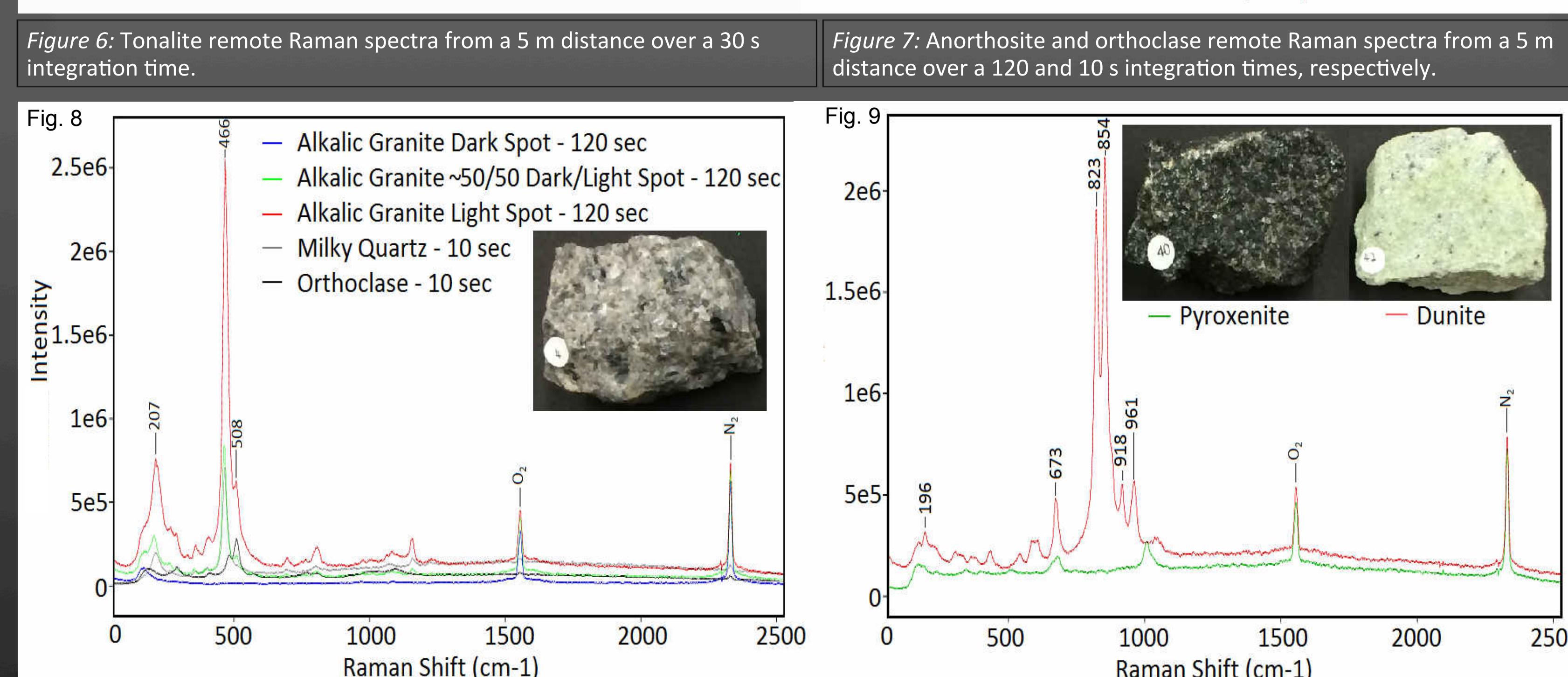
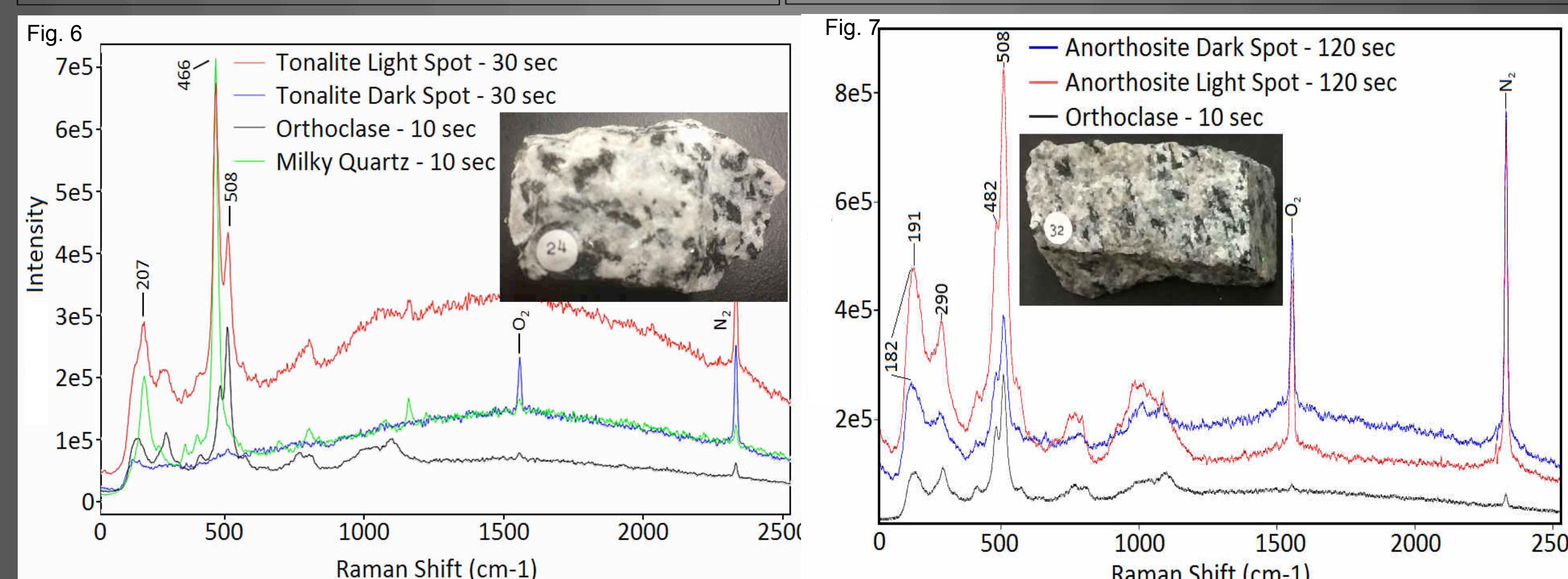
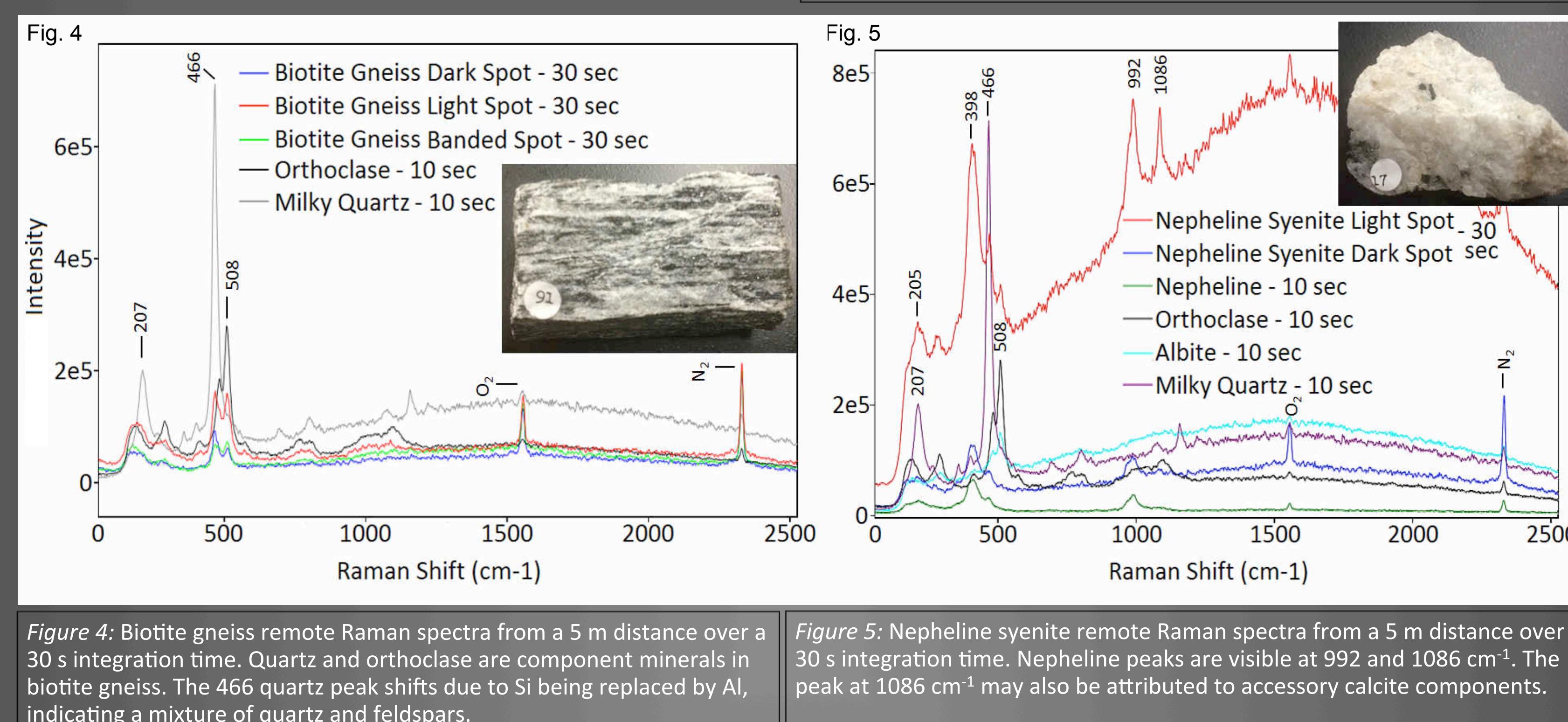
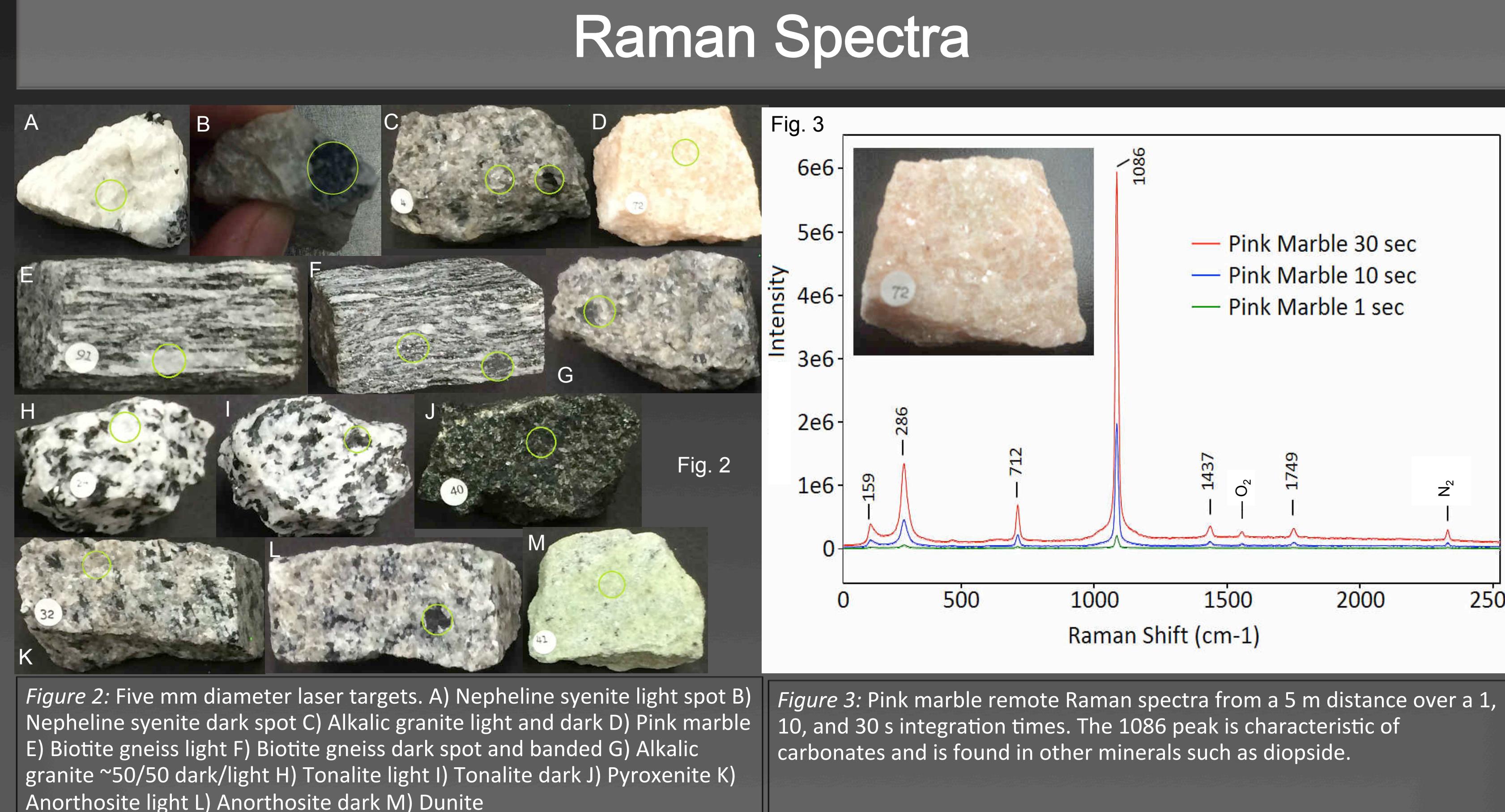
Samples and Instrumentation

The CRRFLS contains a small 532 nm Q-switched frequency-doubled Nd:YAG laser source and an electronically gated custom mini-ICCD detector. The 20 Hz pulsed laser was used at 20 mJ per pulse. It employs a 2.5-inch collection telescope, a 532 nm notch filter, a 50 micron slit, and two stacked volume phase transmission gratings. The compact spectrograph is 10 cm long x 8.2 cm wide x 5.2 cm tall.

Raman spectra were acquired for 30 seconds (600 laser pulses) for pink marble (Tate, Georgia, USA), biotite gneiss (Uxbridge, Massachusetts, USA), nepheline syenite (Bankcroft, Ontario, Canada), tonalite (San Diego County, California, USA), nepheline, orthoclase, milky quartz, and albite. Raman spectra were acquired for 120 seconds (2400 laser pulses) for anorthosite (Elizabethtown, New York, USA), alkali granite (Quincy, Massachusetts, USA), pyroxenite-hazburgite (Stillwater Complex, Montana, USA), and dunite-olivine peridotite (Balsam, North Carolina, USA). Samples were acquired from Ward's Collection of Classic North American Rocks 45-7250. [6] A laser spot diameter of 5 mm was used for all target measurements. (Figure 2)



Figure 1: Compact remote Raman+LIBS+Fluorescence system (CRRFLS) mounted on a movable pan/tilt scanner.



Acknowledgements

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- [1] Wiens., et al. (2016) LPSC, this conf. [2] Misra, A.K., et al. (2011) Proc. SPIE, 8032, 8032Q. [3] Wiens, R.C., et al. (2005) Spectrochim Acta A, 61, 2324-2334. [4] Sharma, S.K., et al. (2010), Phil. Trans. R. Soc., 368, 3167-3191. [5] Garcia, C.S., et al. (2006) Proc. SPIE, 6302, 630215 [6] Misra., et al. (2016) LPSC, this conf. [7] www.wardsci.com

Results and Discussion

Figure 3 shows remote Raman spectra of pink marble (CaCO₃) from a 5 m distance at various integration times. The CRRFLS is capable of fast data acquisition as seen by the detection of Raman lines at 1, 10, and 30 s.

Figure 4 shows remote Raman spectra of light, dark, and both light and dark (banded) areas in biotite gneiss (K(Mg, Fe²⁺)(Al, Fe³⁺)Si₃O₁₀(OH, F)₂). Figure 4 also shows reference remote Raman spectra of pure orthoclase and quartz minerals used to confirm rock mineral components.

Figure 5 shows remote Raman spectra of nepheline syenite ((Na,K)AlSiO₄) at both light and dark spots, along with the remote Raman spectra of nepheline, orthoclase, albite and quartz. The sample shows high levels of fast organic/bio-fluorescence background, particularly visible in the lighter areas. Pure nepheline, orthoclase, milky quartz, and possible albite mineral components, make up the nepheline syenite spectrum. The presence of nepheline is confirmed by the peaks at 398 and 992 Raman shifts. The dark spot analyzed only contains nepheline, and the light spot analyzed contains nepheline, orthoclase, milky quartz, and albite.

Figure 6 depicts remote Raman spectra of tonalite, NaCl, CaO, MgO, SiO₂, (quartz diorite with a quartz content 5-20% of the rock) at a 5 m standoff distance over 120 s integration times. Moderate levels of fast organic/bio-fluorescence background are visible. The tonalite spectrum matches up with plagioclase, orthoclase, and quartz mineral components.

Figure 7 highlights the remote Raman sensitivity between 5 mm diameter targets with slight variances in composition or color. Mafic components such as pyroxene in orthoclase feldspars (K(AlSi₃O₈)) explain the darker spectrum from anorthosites (CaNa₂Si₂O₈).

Figure 8 shows a preliminary visual attempt at a rock mineral component deconvolution using remote Raman analysis on alkali granite dark and light spots and an approximate 50/50 mix. Figure 9 depicts olivine rich dunite and pyroxenite Raman spectra. Olivine peaks are clearly visible at 823, 854, 918, and 961 Raman shifts. Chromite (FeCr₂O₄) and feldspar mineral components are visible at 673 and 196 Raman shifts.

Conclusions and Future Work

We have demonstrated the capabilities of the Compact Remote Raman+LIBS+Fluorescence System (CRRFLS) at a standoff distance of 5 m to analyze natural rocks in daylight conditions and with high fluorescence backgrounds, without sample collection or preparation. The remote Raman analysis is consistent with rock compositions, effectively detecting individual mineral components. Current investigations involve analysis of progressive mineral mixing models with powders and natural rocks to deconvolve natural rock Raman spectra.

Rock	Rock Type	Mineral Components*Strong Detection
Biotite gneiss	High grade metamorphic rock	Banded dark biotite mica lighter feldspar* and quartz*
Nepheline syenite	Intrusive igneous rock	Nepheline* and alkali feldspar*; nepheline reacts with quartz to produce alkali feldspars such as orthoclase*
Tonalite (quartz diorite)	Intrusive igneous rock	Quartz*, biotite, plagioclase* and orthoclase* feldspars
Pink marble	Metamorphic rock	calcite
Orthoclase	Phaneritic igneous rock	Plagioclase and potassium feldspars*, mafic component* including minerals such as pyroxenes and olivines
Anorthosite	Phaneritic intrusive igneous rock	Plagioclase feldspars*, minimal mafic component <10%
Alkali granite	Felsic igneous rock; granite	Quartz*, plagioclase and potassium feldspars*
Dunite	Phaneritic igneous ultramafic plutonic rock	>90% olivine*, pyroxene, chromite*, feldspars*
Pyroxenite	Ultramafic igneous rock	Mostly pyroxene*

Table: Mineral components of natural rocks detected by remote Raman.

References

- [1] Wiens., et al. (2016) LPSC, this conf. [2] Misra, A.K., et al. (2011) Proc. SPIE, 8032, 8032Q. [3] Wiens, R.C., et al. (2005) Spectrochim Acta A, 61, 2324-2334. [4] Sharma, S.K., et al. (2010), Phil. Trans. R. Soc., 368, 3167-3191. [5] Garcia, C.S., et al. (2006) Proc. SPIE, 6302, 630215 [6] Misra., et al. (2016) LPSC, this conf. [7] www.wardsci.com