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Multi-Modal Identification of Feldspar and Iron Oxide Phases in Granite Using Raman Spectroscopy in the Electron Microscope

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Scanning electron microscopy (SEM) with energy-dispersive x-ray spectroscopy (EDS) is one of the most versatile methods for identification of micro-scale material phases of differing elemental composition. However, it is not very helpful in differentiating structural differences or crystal polymorphism, so getting full information about a material usually involves combining SEM-EDS with a complementary structural analysis technique. It is often paired with electron backscatter diffraction (EBSD), electron diffraction, or x-ray diffraction depending on the size of the features and type of material. Though it is much less common, there are now also commercial solutions for Raman spectroscopy in the electron microscope. Raman spectroscopy can be used on a variety of materials to obtain a characteristic spectrum for identification or information on the crystal structure or molecular bonding [1]. Relevant to this work, Raman spectroscopy has been used to differentiate feldspar and iron oxide minerals [2, 3] with characteristic Raman spectra available through both public online databases and commercial spectral libraries [4-7].

This paper shows how multimodal analysis in the electron microscope using Raman spectroscopy and SEM-EDS allows positive identification of several phases in granite at length scales of tens of microns down to sub-micron. The Raman spectroscopy tool used here is a pre-production prototype system designed by Thermo Fisher Scientific and installed at the University of Cincinnati Advanced Materials Characterization Center as an attachment to the Scios DualBeam. A piece of granite from Madison, WI with an overall pink color indicative of high K-feldspar content was sectioned, mounted in epoxy, and polished for analysis. Figure 1 shows an area with an inclusion visible in the secondary electron and optical images. SEM-EDS was done at 10 kV accelerating voltage to get a composite EDS map of Fe (red), Na (blue), and K (green) x-ray intensity maps and Raman spectroscopy maps were also taken of the area using a 20× objective with 5 µm pixels for the overview map and 1 µm pixels for the inset map. The inset region was replotted for peaks of interest shown in Fig 3.

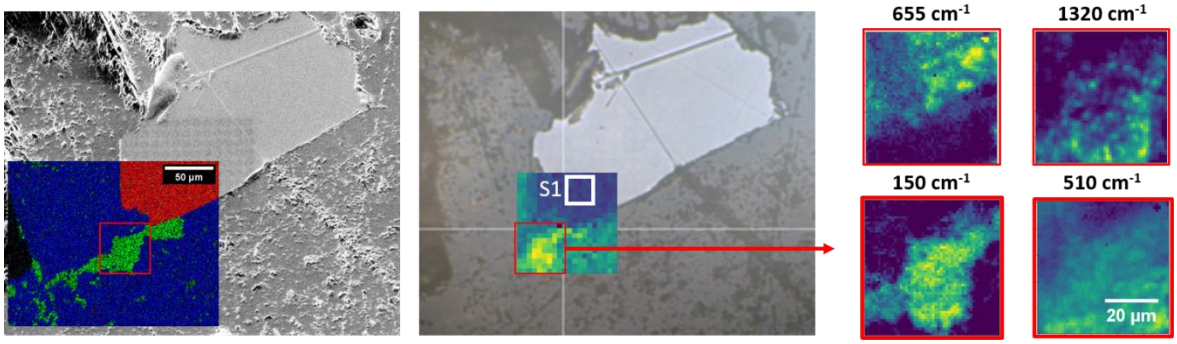

Figure 1. SEM image with overlaid EDS map (left), optical image with overlaid Raman map (middle), and Raman map using 20× objective and 1 µm pixel size replotted for four peaks of interest (right).

The Raman maps in Figure 1 showed what appeared to be inclusions with a characteristic peak around 1320 cm^{-1} dispersed within a main phase that has a strong peak at 150 cm^{-1}. There was also a fairly uniform background of the 510 cm^{-1} peak with some areas having a peak at 650 cm^{-1}. These features were compared with a geological spectral database and the phases in question were identified as albite in the Na-rich phase, microcline in the K-rich phase, magnetite in the large Fe-rich inclusion, and hematite in the micro-scale inclusions with a peak at 1320 cm^{-1}. To confirm whether these inclusions were in fact a distinct phase, a higher resolution map was taken with a 100× objective and 200 nm pixels in the potassium rich area as shown in Figure 2. The spectrum characteristic of hematite with large peak near 1320 cm^{-1} was extracted from the sub-micron particles observed in this map. The morphology of these nanoscale inclusions could be most conclusively confirmed with high resolution STEM imaging.

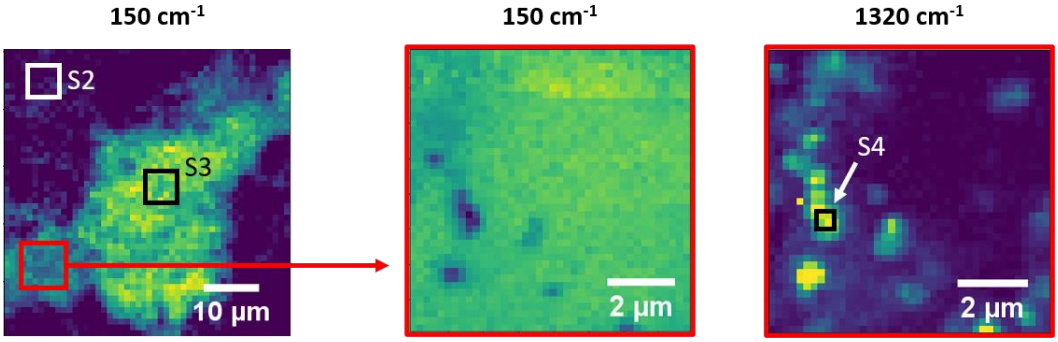

Figure 2. Raman map using 100× objective and 200 nm pixel size taken in the K-feldspar region and plotted for the 150 cm^{-1} and 1320 cm^{-1} Raman peaks. Comparison with the reference spectra confirms that this is a region of primarily microcline with sub-micron hematite inclusions.

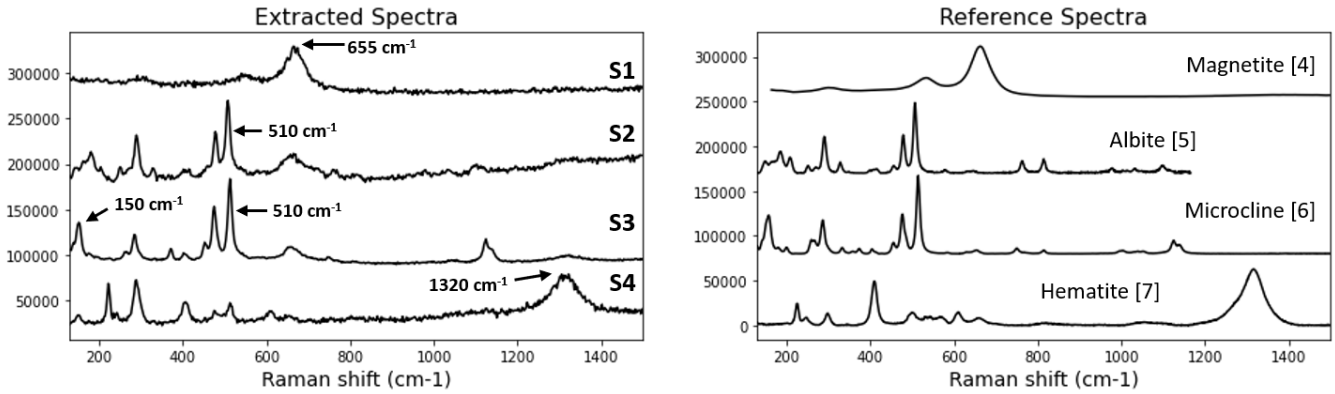

Figure 3. Plot of the Raman spectra (S1-S4) extracted from the regions shown in Figs. 1 and 2. The characteristic peaks of interest at 150 cm^{-1}, 510 cm^{-1}, 655 cm^{-1}, and 1320 cm^{-1} are shown. The spectra match well with reference spectra for magnetite, albite, microcline, and hematite.

This investigation showed SEM-EDS paired with Raman spectroscopy to be a useful technique for identifying mineral phases at length scales from tens of microns to sub-micron. Although SEM-EDS made the identification of the primary Fe-rich and feldspar phases trivial, it was not as helpful in identifying the micro-scale hematite inclusions present in the K-feldspar region or the specific

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polymorphs of the plagioclase feldspar or the K-feldspar. Raman spectroscopy is therefore presented as a useful complementary technique to SEM-EDS, especially given the minimal sample preparation needed for both Raman and EDS as opposed to the exacting requirements for surface quality for EBSD, large length scales of x-ray diffraction, and time consuming workflow for electron diffraction. Lamella preparation and electron diffraction will of course continue to be the most authoritative final identification tool for nanoscale inclusions such as those identified here using Raman spectroscopy [8].

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[8] The authors gratefully recognize NSF MRI grant #1531593 in support of purchasing the Scios DualBeam system allowing the present work.