Application of Raman Microscopy to Fluid Inclusions in Minerals

**Key Words**
Confocal Raman Spectroscopy, Fluid Inclusions, Geology, Mineralogy, Raman Spectroscopy

**Overview**
Fluid inclusions are small, sealed, naturally occurring volumes found in mineral host crystals containing encapsulated aqueous and non-aqueous liquids and gases. Discrete mineral phases may also occur within fluid inclusions, either by precipitation from the solute-rich fluids or via collocation at a host crystal defect. Fluid inclusions appear in many different patterns. For example, fluid inclusions can be found isolated in a host crystal trapped during initial crystallization or in trails along former micro-fractures or grain boundaries. The study of the abundance, orientation, and chemistry of fluid inclusions provides a rich history of formation and alteration over time, contributing to both fundamental studies of geologic processes as well as practical assessments of economic value.

The analysis of fluid inclusions in any rock sample begins with preparing a double-sided polished thin section for transmitted light microscopy and microthermometric studies. Samples prepared in this way are also ideal for non-destructive analysis using a confocal Raman microscope. A confocal Raman microscope, like the Thermo Scientific DXR Raman microscope, uses an optical arrangement that inserts a limiting aperture at an image plane. This approach serves to limit the Raman signal entering the spectrograph to a very specific, sharply in focus, volume in the sample. The resulting Raman spectrum is characteristic of that isolated region alone, eliminating or strongly reducing Raman signals from out-of-focus regions in the field of view. By definition a fluid inclusion is surrounded by a host mineral, yet a Raman spectrum of the contents of the inclusion alone can be obtained by focusing at a plane inside the specimen and bringing the inclusion into focus. The analysis is completely non-destructive, and spectra of volumes as small as a few microns in size can be obtained. Figure 1 is a typical view of a thin section showing a relatively large inclusion containing fluids partitioned into two phases. Nearby, a trail of very small inclusion is visible. There are actually several trails, stacked nearly vertically. Adjusting the focus of the microscope will bring trails at different planes into focus for confocal Raman analysis.

Figure 1: Different inclusion habits and principle of confocal focus control, 100× objective
Applications
All spectra in the note were produced with a DXR™ Raman microscope, 100× objective, and 532 nm laser excitation. Spectra were collected in confocal mode with a 25 micron pinhole aperture. Table 1 indicates the primary Raman band associated with common gases and the oxyanions of solutes associated with fluid inclusions. The position of the peaks can be influenced by pressure, temperature and – in the case of water and the oxyanions – the salinity and specific counter ions present. It is very important to be confident of the wavelength calibration of the spectrometer system so that spectral shifts observed can be appropriately attributed to the physical or chemical environment and not a shift in calibration. An autocalibrating spectrometer system such as the DXR microscope is much preferred for data integrity.

<table>
<thead>
<tr>
<th>Gases</th>
<th>SO₂</th>
<th>CO₂ (g)</th>
<th>CO</th>
<th>N₂</th>
<th>H₂S</th>
<th>CH₄</th>
<th>H₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raman Shift cm⁻¹</td>
<td>1151</td>
<td>1285/1368</td>
<td>2143</td>
<td>2331</td>
<td>2611</td>
<td>2917</td>
<td>4156</td>
</tr>
</tbody>
</table>

Table 1A: Nominal Raman shift frequencies of common fluid inclusion species

<table>
<thead>
<tr>
<th>Solutes</th>
<th>SO₄²⁻</th>
<th>NO₃⁻</th>
<th>HCO₃⁻</th>
<th>CO₃⁻</th>
<th>CO₂(l)</th>
<th>B(OH)₃</th>
<th>H₂O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raman Shift cm⁻¹</td>
<td>980</td>
<td>1049</td>
<td>1050</td>
<td>1064</td>
<td>1384</td>
<td>877</td>
<td>2800-3900</td>
</tr>
</tbody>
</table>

Table 1B: Nominal Raman shift of oxyanions (counter ion dependent)

A number of solutes may be observed in the aqueous phases of inclusions directly by Raman spectroscopy, but there is also indirect evidence of species without Raman spectra, such as sodium and potassium ions in solution. The spectrum of water coordinated to the cations changes the shape of the O-H stretching region as shown in Figure 4. The changes in the O-H region may be used to predict the salinity of the fluid, and when combined with freezing point data the cation species can be predicted. The spectrum of the OH stretching in this fluid clearly shows it is water, however the spectrum of the O-H region actually is comprised of three different modes that vary in relative intensity depending on salinity of the phase.

Figure 3: Gas phase species in inclusion trail indicating reducing conditions at entrapment
Solid phases within inclusions may be identified with confocal Raman microspectroscopy. The image of the inclusion in Figure 5 has a light colored, solid feature visible along its lower boundary with the host crystal. The spectrum of the solid was first isolated by using spectral subtraction to remove Raman bands of the host crystal (quartz). Searching the subtraction result against a data base of mineral spectra immediately identified the particle as a mica group mineral. Figure 5 shows the processed spectrum of the particle compared to a muscovite reference spectrum. Based on the history of the formation and small grain size, this particle is likely sericite, a mineral very similar to muscovite. Studying the interfaces between the particle, liquid phase, and host crystal with confocal Raman spectroscopy confirmed the sericite particle is embedded in the inclusion wall. Therefore this inclusion formed around the sericite particle, rather than the particle forming within the inclusion.

The photograph in Figure 6 is an example where the solid quite clearly formed from the solutes in the trapped liquid. The translucent solid moves freely in the fluid. Solids with the same Raman spectrum were found in other inclusions in the specimen, adding confidence to the assumption the mineral formed from aqueous phase constituents. The thin section is from a pegmatite formation that typically crystallizes from boron rich melts that explains the borate in solution and the boric acid-like peak at 882 in the solid phase. The gas phase is CH4-CO2, saturating the solution with carbon dioxide and forcing significant concentration of bicarbonate. The cluster of peaks in the between 1013 and 1038 might be from bicarbonate salts. A search for minerals with bicarbonate/borate composition with a published Raman spectrum lead to a single candidate. The spectrum of mineral qilianshanite, NaH4(CO3)(BO3)·2H2O, is a very good match to this solid and is consistent with the composition of the inclusion (see ruff.info spectrum ID R100019).

**Summary**

The confocal capabilities of the DXR Raman microscope are ideal for characterizing the contents of fluid inclusions. The system is designed for robust alignment and calibration making it especially attractive to scientists that use many different techniques in their research. You need not be an optics expert to obtain reliable, very high quality data. The availability of database searching, curve fitting, and other computation tools in Thermo Scientific OMNIC software allows identification of unknown mineral phases and spectra-based physical interpretations such as salinity and density of fluids.