

Raman Mapping of Mineral Inclusions in Diamonds and other Mineral Samples

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DXR Raman Microscope, Geology, Inclusion, Mineral, Non-destructive Analysis, Raman Spectroscopy

Introduction

Raman spectroscopy is a relatively easy technique that can be used to analyze inclusions within minerals because very little sample preparation is required and the Raman signal from the mineral matrix can often be excluded from the signal of the inclusion. Raman spectroscopy is also advantageous because of the high spatial resolution that is possible, especially when compared with X-ray diffraction and other analytical methods. In this application note, we present an interesting and powerful alternative method to analyze inclusion within diamond and other mineral samples.

Mineral inclusions are important in petrology because their entrapment often shields them from later processes and allows the early stages of an igneous or metamorphic event to be observed. It is often beneficial to identify mineral inclusions before they are exposed at the surface, but this is usually challenging because their small size precludes optical identification, and routine analytical techniques such as scanning electron microscope (SEM) based X-ray spectroscopy are limited to surfaces. Mineral inclusions tell us about the earlier stages of evolution of the rock: in metamorphic rocks they can preserve early fabrics and minerals that have subsequently been removed from the matrix of the rock by metamorphic reactions. In lavas, mineral inclusions can be extremely useful in determining the conditions of equilibration of the minerals. For example the compositions of plagioclase inclusions in hornblende can help constrain the pressure (i.e. depth below the surface) and temperature of the magma chamber, which could allow the eruptive potential of the volcano to be estimated.¹ In ore bodies, sulphide melts can be trapped along fractures in quartz; the cracks subsequently 'heal', leaving numerous minute mineral inclusions distributed along a plane within a single quartz crystal. The small size of these inclusions



can make it difficult to expose them for analysis, and their dispersed nature means only a few can be exposed at a given time.

As noted earlier, electron beam techniques such as SEM and electron probe rely on the material being exposed at the surface. For some materials this is not practical, either because of the time required, the need to avoid chemical contamination of the inclusion that could occur during polishing, or because the material is rare and cannot undergo destructive preparation procedures. Infrared spectroscopy could in some cases be used to identify mineral inclusions, but would require double-polished wafers that are often impractical to prepare. Synchrotron-based X-ray fluorescence methods have been applied to mineral inclusions in diamonds (e.g. Brenker et al, 2007), but are not feasible for routine work.²

Experimental

Samples were prepared using standard petrological techniques (polishing with a diamond-impregnated scaife for the diamonds, polishing with SiC and diamond suspension for all other samples). Raman spectra and maps were obtained using a Thermo Scientific™ DXR™ Raman microscope. A 532 nm laser providing between 3 and 8 mW at the sample surface was used to obtain all spectra. Reflected and transmitted light optics were used to select analysis locations. Point spectra were collected for between 20 and 50s depending on the sample. The map was obtained in confocal mode using a 25 μm pinhole to limit the unwanted signal from the surrounding diamond; spectra (50s each) were obtained from a grid of points spaced 2 μm apart, resulting in a total acquisition time of ~13 hours. Because the mapped inclusion was at a depth of ~100 μm in the diamond, a 50 \times long working distance objective lens was used to prevent contact between the diamond and the lens whilst maintaining high spatial resolution.

Results and Discussion

Inclusions in Diamond

Diamond often contains mineral inclusions of geological interest. Because diamond is the hardest known material, polishing down and exposing these inclusions is time-consuming and often costly. Raman spectroscopy allows inclusions to be identified whilst they are still encapsulated in the diamond, because of the confocal advantage and high spatial resolution that Raman

microscopy offers. Utilizing confocal Raman microscopy to analyze below the surface is especially useful when exposing an inclusion might contaminate it and prevent further analysis, as is the case with isotopic analysis.

The inclusion illustrated in Figure 1 (field of view 0.25 mm) is coesite, a high pressure polymorph of SiO_2 . This is a sign that the diamond crystallized in association with subducted oceanic crust. The Raman spectrum of this sample is shifted slightly with respect to that recorded from a coesite standard because the inclusion is still experiencing a pressure of 2.2 GPa.³

Some inclusions in diamonds formed at extremely high pressures, near the base of the upper mantle. Although they formed as single crystals, they became unstable during their ascent in a mantle plume and have decomposed into multiple phases. Figure 2 shows an inclusion that formed as part of the $\text{Ca}(\text{Si,Ti})\text{O}_3$ perovskite solid solution but subsequently broken down to form a large colorless crystal of CaSiO_3 and several small reddish-brown crystals of CaTiO_3 . The Raman map allows us to distinguish the two and confirm that no other phase is present. Being able to demonstrate the presence of both minerals is conclusive proof of the ultra-deep origin of this sample: whilst CaSiO_3 and CaTiO_3 are both stable over a wide range of pressures and temperatures, the solid solution $\text{Ca}(\text{Si,Ti})\text{O}_3$ is only stable at pressures >12 GPa at typical mantle temperatures.⁴

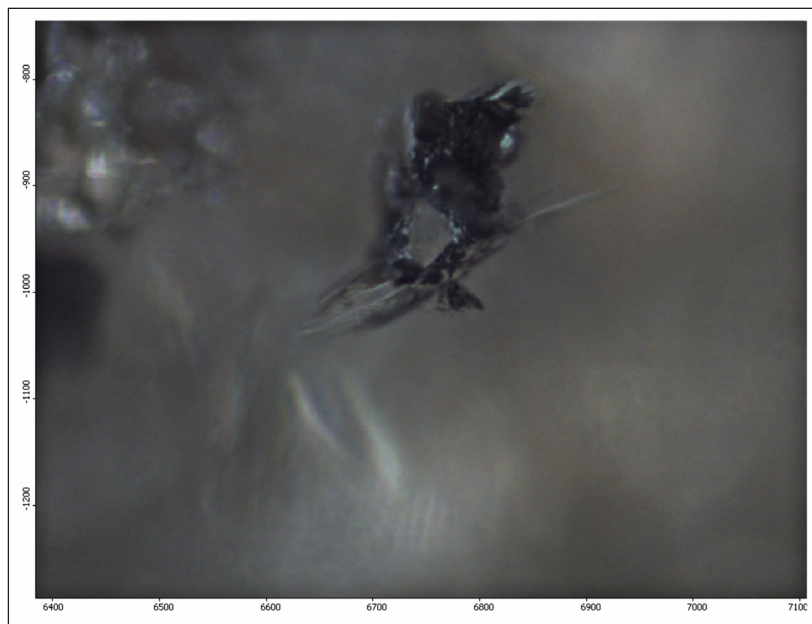
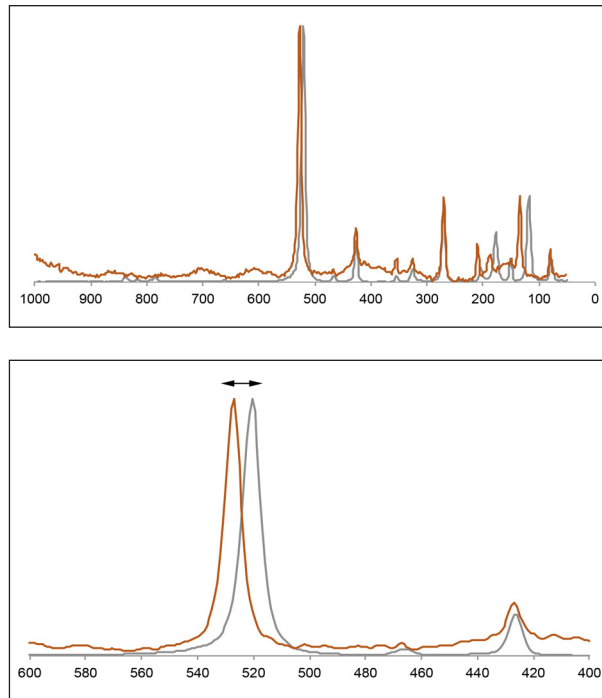


Figure 1: A coesite (SiO_2) inclusion in a diamond. The small offset of the observed Raman spectrum (orange) from a reference spectrum obtained from a synthetic standard (grey) occurs because the inclusion is trapped at a pressure of ~2.2 GPa by the rigid diamond lattice.



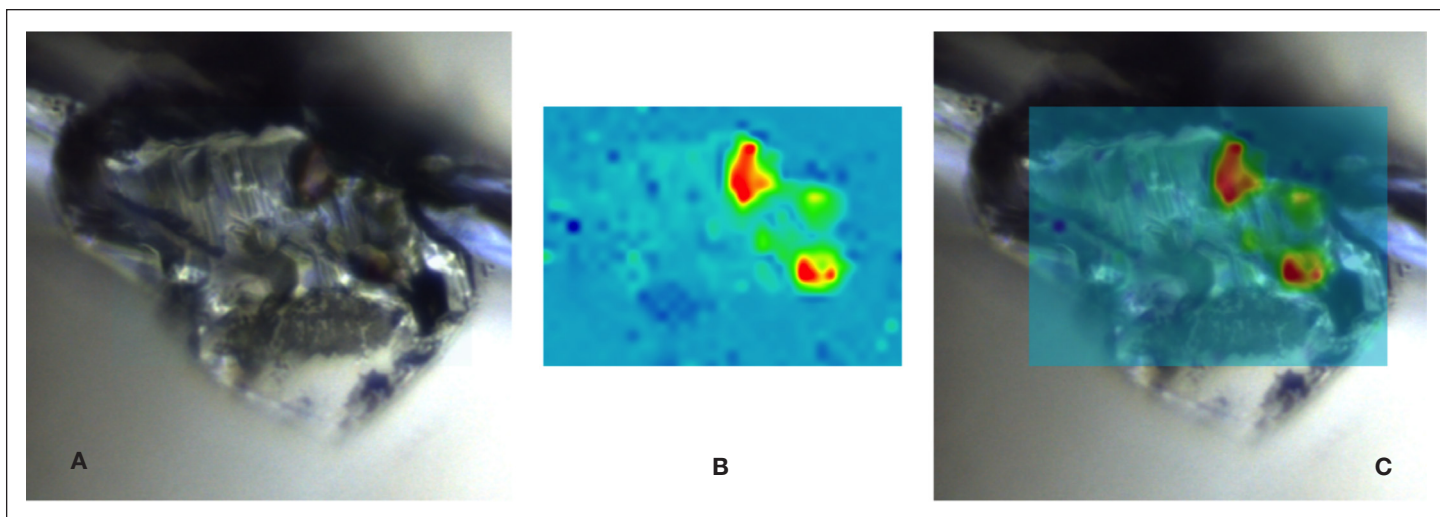


Figure 2: A composite inclusion in a diamond, interpreted to have formed as a single grain of $\text{Ca}(\text{Si,Ti})\text{O}_3$ perovskite in the transition zone of the Earth's mantle. a) Photo; b) Raman intensity at 342 cm^{-1} (characteristic of CaTiO_3); c) Comparison of the two. Field of view in photo is ~ 120 microns.

Thin Sections with Cover Slips

Many thin sections have been preserved with cover slips, and thus present a similar analytical challenge as unexposed mineral inclusions. As with unexposed mineral inclusions, confocal Raman spectroscopy allows us to see past the cover slip and epoxy and analyze the minerals underneath. For example, the eclogite, which is the rock type that basalt becomes during high pressure metamorphism illustrated in Figure 3, (field of view 0.7 mm wide) contains a brown mineral and a colorless, low relief, low birefringence mineral: challenging optically (e.g. the colorless mineral could be albite, quartz or several other minerals), but Raman shows them to be rutile and albite respectively. Correct mineral identification is essential to determining the conditions of formation of the rock: in eclogites the presence of free quartz is controlled in part by the pyroxene composition, which varies with pressure and temperature.

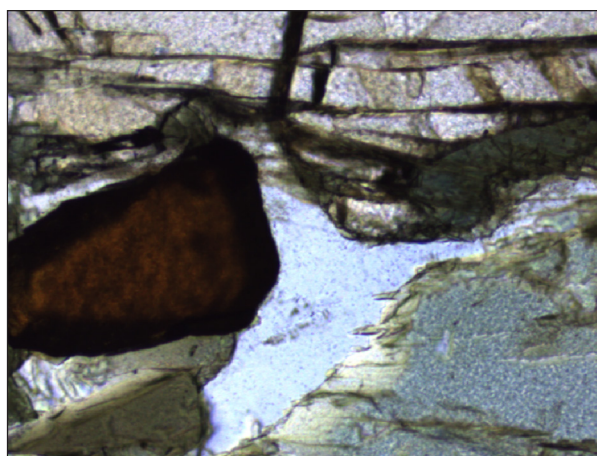


Figure 3: Photomicrograph of an eclogite from Glenelg, Scotland. The green minerals are omphacite and hornblende, the pink mineral is garnet, and the brown and colorless minerals were initially not known. Raman spectroscopy through a coverslip allowed their identification as rutile and albite respectively. Field of view 0.75 mm.

Melt and Fluid Inclusions

Raman spectroscopy can also identify the volatile contents of fluid and melt inclusions. Fluid inclusions are particularly challenging to study by other techniques because their contents are volatile and disappear as soon as the inclusion is breached by polishing. As an example of the power of Raman spectroscopy, Figure 4 shows fluid inclusions found in a zircon crystal from Amitsoq, Greenland. Rocks at this locality are among the oldest known crustal material on Earth, with ages up to 3.6 billion years old. Raman spectroscopy demonstrates that these inclusions are very CO_2 -rich, which is an interesting constraint on early crust-forming processes. Additional details of confocal Raman studies of this type of sample can be found in application note #52339, *Application of Raman Microscopy to Fluid Inclusions in Minerals*.

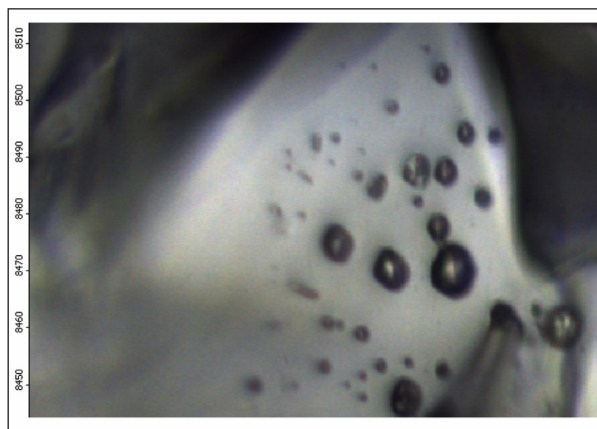


Figure 4: Amitsoq CO_2 vapor inclusions

Conclusions

Raman spectroscopy provides a wealth of information about the composition of microscopic mineral and fluid inclusions within minutes. This is a non-destructive process that only requires normal petrological preparation procedures. The information obtained in this way can constrain the origins of the material being studied, as well as indicating targets for future analysis by alternate methods (e.g. identifying accessory mineral phases that are important for trace element or isotopic studies).

References

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