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Combined SEM and Raman spectroscopy
A new analytical tool for geology and mineralogy
- analysis of sandstone

Introduction

The Renishaw structural and chemical analyser (SCA) shown in Figure 1 allows geologists and mineralogists to benefit from the imaging and analytical capabilities of scanning electron microscopes (SEMs) whilst combining the chemical and structural characterisation provided by Raman spectroscopy. The SEM-Raman system is unique, allowing both rapid observation and elemental analysis at macro and micro scale. An overview and detailed classification of the sample is now available in a single instrument.

Geologists study minerals within rocks to understand the origin of the Earth and the processes that shape or have shaped it: understanding the past is the key to the present.

Figure 1
The SEM-SCA at Bologna University - Italy

The petrographic microscope has been the principal tool for geologists and mineralogists for many years, and can reveal much about a sample, but only if it transmits light.

Opaque minerals need to be studied using other methods like x-ray crystallography and mass spectrometry. Increasingly SEMs fitted with energy dispersive x-ray analysis systems (EDS) are being used, but even instruments fitted with wavelength dispersive X-ray (WDS) analysers are often unable to carry out an unambiguous chemical identification.

Raman spectroscopy measures the vibrational frequencies of molecular bonds in the material being analysed. The resultant Raman spectrum is not only unique for a given compound, but is also sensitive to the local environment. This means the spectra can also reveal structural data. More information about the SCA, and the general theory of Raman and optical spectroscopy, are available in product note SPD/PN/096 (www.renishaw.com/spectroscopy).

Raman spectroscopy uses a focused laser spot as the excitation source; the analysis is unaffected by the vacuum condition and is non-destructive. The laser spot size is in the order of one micrometre, giving a spatial resolution comparable to that of EDS analysis.

SEM-Raman investigation of sandstone from Loch Torridon

The sandstone deposits in the Loch Torridon area of NW Scotland (Figure 2) are amongst the oldest in Europe and were themselves formed from rocks that predate life. A standard geological thin section taken from the sample comprises both transparent and opaque components (Figure 3). This sample is typical of alluvial deposits, and identifying its components can give insight into sedimentation processes and the origins of the host strata.
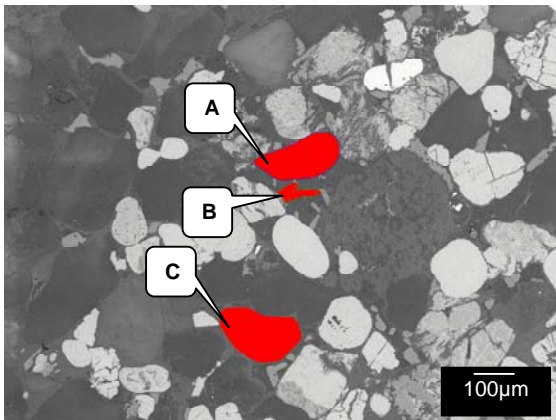

Figure 2
Loch Torridon (photo by permission www.SteveCarter.com)
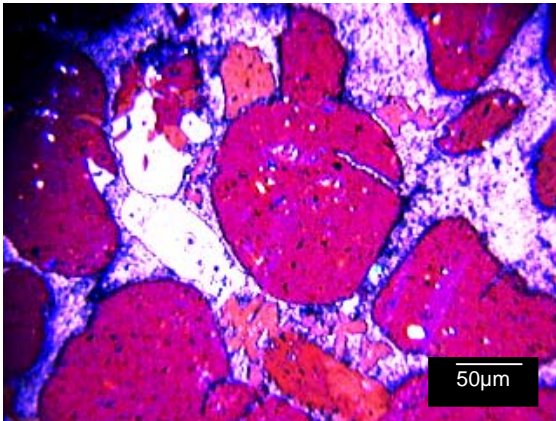
Figure 3
**Optical micrograph of typical part of the sandstone**

The sample was uncoated and non-conductive, and so to avoid charging artefacts in the SEM images it was examined using low vacuum (LV) mode. Under these conditions the contrast in the image arises from differences in the mean atomic number of the components. The brighter a component appears the higher its mean atomic number. Figure 4 shows the area that was selected for investigation using x-ray and Raman spectroscopies.

Figure 4
LV-SEM image showing the image used for x-ray mapping and the areas from which Raman spectra were collected

X-ray maps were collected from the area in Figure 4 - to reveal the spatial distribution of the **elements** within the sample. Whilst the data can be quantified this may not reliably identify oxides and hydroxides, nor can it discriminate between different crystalline forms of the minerals present.

Figure 5 shows the iron, titanium, and potassium x-ray maps collected from the area shown in Figure 4 - these are shown in red, green, and blue, respectively. The x-ray maps were used as a guide to select regions of interest from which Raman spectra were collected.


Fe
Ti
K
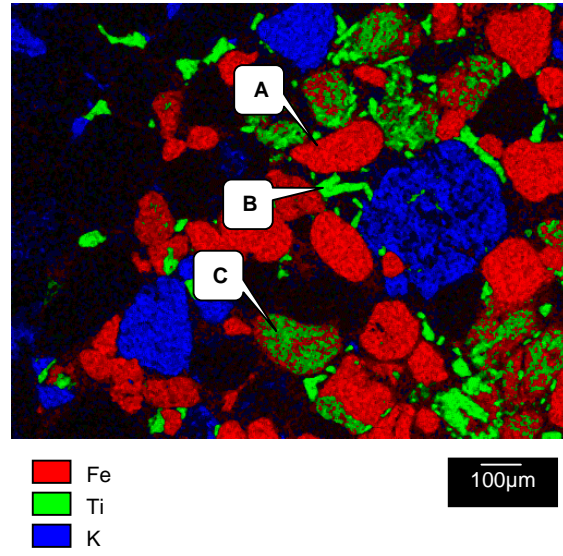
Figure 5
Iron, titanium, and potassium x-ray maps collected from the area shown in Figure 4

Raman spectra collected from regions A, B, and C are shown in Figure 6, 7, and 8 respectively. Using the Renishaw database of minerals, Raman spectroscopy identifies region A as **haematite** – Fe_2O_3
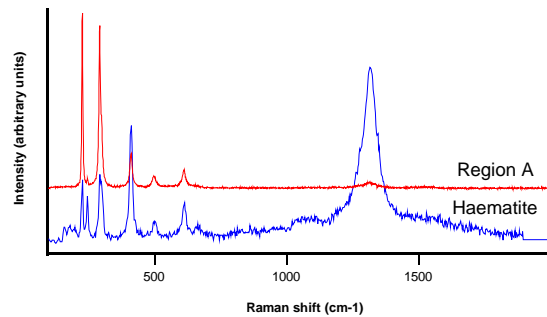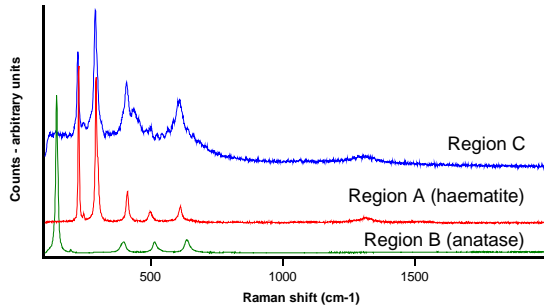

Figure 6
Raman spectrum from Region A (red) and a haematite reference spectrum (blue)

Similarly region B is identified as **anatase**, a polymorph of titanium dioxide (TiO_2).
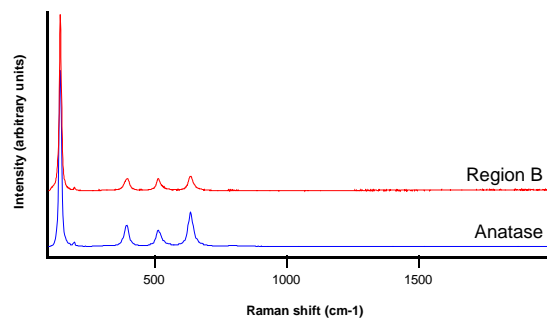
Figure 7
Raman spectra from Region B (red) and an anatase reference spectrum (blue)

The spectrum from Region C (shown in blue in Figure 8) is similar to haematite (in red in Figure 8), but generally less well defined - the peaks are broader and less intense, and there is an extra band at 436 cm^{-1}.
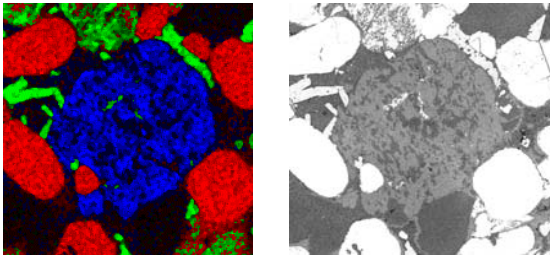

Figure 8
Raman spectra from Regions A (red) B (green) and C (blue)

It is believed that titanium is substituting for iron in the haematite matrix, this could account for the side band at 436 cm^{-1} and is consistent with the x-ray data.

The titanium is not present as anatase though, since the characteristic and very intense anatase Raman bands (green spectrum in Figure 8) are absent, nor do the bands match ilmenite (FeTiO3 – not shown). The peak broadening - characteristic of poor crystallinity - further supports the theory of matrix disruption.

This incorporation of titanium within the haematite matrix implies a complex and extended deposition process.

Figure 9
Potassium x-ray map (blue) from the region shown right

The large grey region shown in Figure 9 comprises two distinct phases as seen in the LV-SEM BE image. These could not be seen in the white light image. X-ray mapping showed the only difference between the phases was the amount of potassium present. Although the phase domains are small (typically < 10 micrometres), the high spatial resolution of the SCA enables spectra to be collected from them. These analyses showed obvious spectral differences between the light and dark areas (Figure 10).

Comparison of the data with library spectra identified both regions as types of feldspar. The darker regions were specifically classified as **plagioclase feldspar**, and the lighter ones as **alkali feldspar** – this is consistent with the x-ray data.
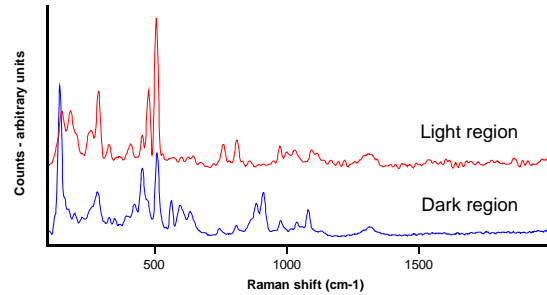
Figure 10
Raman spectra from the dark (blue) and light regions (red)

The exsolution structure noted in the feldspar indicates rapid cooling of the parent igneous rock

In this example combining Raman spectroscopy with SEM imaging and EDS analysis has enabled the minerals and their phases to be fully characterised.

This would not have been possible using optical microscopy alone because the opaque minerals cannot be identified. Similarly x-ray analysis used in isolation would have given a misleading result for the titanium-substituted haematite, and would not have identified the titanium dioxide polymorph or the feldspar chemistry.

X-ray mapping, however, is an effective technique for locating regions of interest, and identifying the elements present within them. This data can assist greatly with interpretation of the Raman spectra, which can be very sensitive to subtle chemical and structural differences.

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Advantages of SEM-SCA in geology and mineralogy

- Raman determines the chemical composition whereas EDS just identifies the elements present

- Raman can distinguish between polymorphs whereas EDS cannot (e.g. rutile, crystobalite)

- The laser and SEM spot size allows better spatial resolution than optical petrography

- Raman analysis can be carried out *in situ* so that the spatial context is maintained

- EDS analysis and Raman spectroscopy complement each other by revealing subtle variations in composition or the presence of trace elements

- Standard thin sections can be viewed without additional preparation permitting their re-use by optical petrography

- Full characterisation of economic and opaque minerals can be carried out quickly and easily

Why choose Renishaw?

Renishaw is an established world leader in metrology, and has been providing high performance solutions for measurement and control since 1973. In 1992, Renishaw combined several new technologies, including its metrology expertise, into its Raman microscope and rapidly became a world leader in the design and manufacture of Raman spectroscopy systems. Renishaw has a global network of subsidiary companies, distributors, and agents, providing a level of service second to none. Its teams of highly qualified engineers and scientists can provide you with rapid and comprehensive product, technical, and application support.