

Combined SEM and Raman spectroscopy A new analytical tool for geology and mineralogy - analysis of heavy mineral sands

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.

Process control monitoring is an important part of commercial minerals extraction. Failure to recognise deterioration in process efficiency can have significant financial implications. Conversely, any improvements to the process can reap rewards in a short space of time.



Figure 1
The SEM-SCA at Bologna University - Italy

Traditionally for industrial scale extraction, efficiency is evaluated by comparing the final yield with the amount of starting material consumed. Increasingly though, this rather unsatisfactory method is being replaced by in-stream monitoring. This enables efficiency to be regularly monitored so that process deterioration can be picked up at an earlier stage, and measures implemented to improve the process.

SEM-Raman investigation of heavy mineral sands



Heavy mineral concentrates from placer sand deposits on the east coast of South Africa are a valuable source of titanium, zirconium, and iron. Flotation, magnetic, and electrical separation methods are used to concentrate the sands into Ti-rich, Zr-rich, and Fe-rich streams. The efficiency of this process has previously been investigated using SEM and X-ray analysis, and conventional Raman microscopy. This approach was valuable, but examination of the same region of interest in different instruments was not practical.

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 (energy dispersive x-ray analysis).

Conventional Raman microscopy has been used previously to identify the composition of grains. This has proven time-consuming because the grains look similar when examined optically so that many need to be analysed before statistics regarding the composition can be considered reliable (see Figures 2 and 3 for example). Stage mapping in combination with autofocus can overcome most of the sample-size related difficulties; but these methods require careful setting up, and long acquisition times to yield representative data.

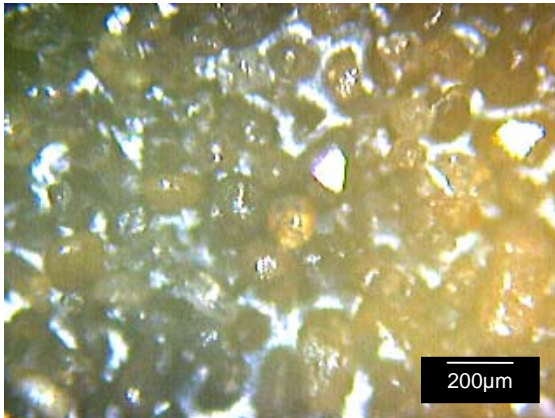


Figure 2
Optical microscope image collected from a typical area using 5x objective

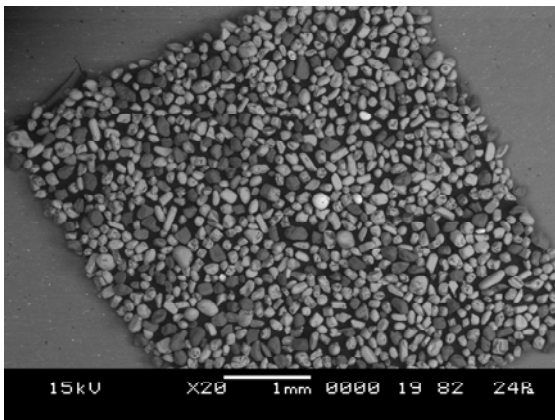


Figure 3
Low magnification LV-SEM image of prepared sample

This investigation used the SEM-SCA to carry out SEM, EDS, and Raman spectroscopy *in situ* to enable both classification **and** chemical identification to be carried out more rapidly.

The sample was taken from a zirconium-rich stream, and was prepared simply by sprinkling the sand grains onto an adhesive pad and then shaking off any non-adhering particles. The sand grains are non-conductive and so the SEM was used in low-vacuum mode to avoid charging. In this mode the image contrast comes predominantly from differences in mean atomic number – denser particles appear brighter. Figure 4 shows a higher magnification

image from the centre of Figure 3 and was also the area from which the x-ray maps were collected.

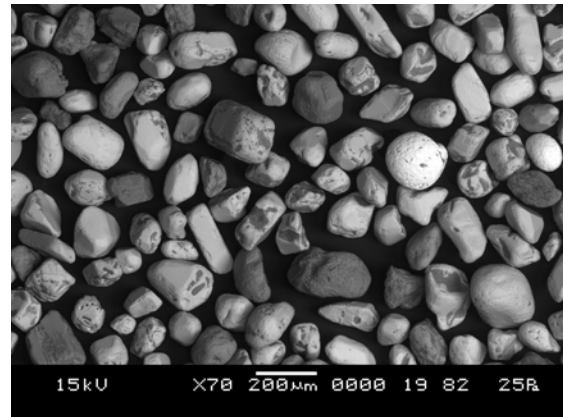


Figure 4
LV-SEM image from the centre of Figure 3 – this was the area from which x-ray maps were collected

X-ray mapping of the sample in the SEM identifies the elements present within a few minutes, and allows the sample to be **classified** - namely the fraction of impurities (in this case titanium grains) in the zirconium-rich stream. X-ray analysis alone, however, often cannot identify unambiguously the precise chemical composition of the grains.

Almost a dozen elements were detected within the region shown in Figure 4, but only the most abundant ones are considered here. Figures 5 and 6 show x-ray maps for zirconium and titanium. The majority of particles analysed contain zirconium, some contain titanium, whilst a small minority of others contain neither zirconium nor titanium - these will be considered later.

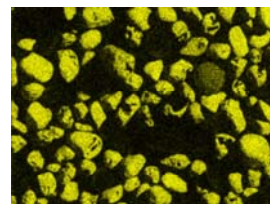


Figure 5
Zr map from the region shown in Figure 3

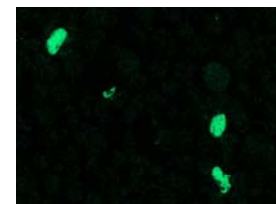


Figure 6
Ti map from the region shown in Figure 3

The Renishaw SCA enables Raman spectroscopy to be carried out inside the SEM. The principal advantage of this capability in this example is that grains of interest, located using SEM imaging and x-ray analysis, can be characterised **chemically** using Raman spectroscopy. Figure 2 shows how the sample appears to the light microscope. Comparing this to a similar magnification SEM image (Figure 4 for example) illustrates how difficult it can be to relocate grains of interest identified in the SEM with an optical microscope based spectrometer.

In-situ Raman spectra (Figure 8) recorded from typical titanium and zirconium containing grains (see the red and green particles in Figure 7 respectively), was followed by spectral matching against Renishaw's minerals library. This showed that the particles comprise **rutile** (red spectrum) – a polymorph of titanium dioxide (TiO_2), and **zircon** (ZrSiO_4) – the blue spectrum.

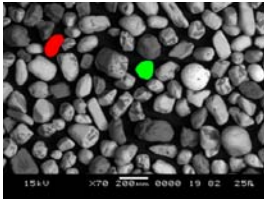


Figure 7
Figure shows areas where Raman data were collected

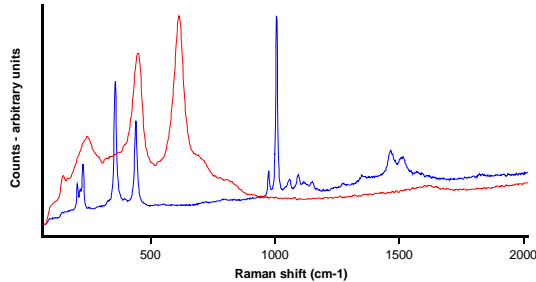


Figure 8
Raman analyses of the areas shown in Figure 7

These results, combined with the x-ray mapping data shown in Figures 5 and 6, give a measure of the purity of the zirconium-rich stream.

There are some grains, however, that are neither pure rutile nor zircon and these are also of interest.

The bright particle coloured red in Figure 9 below (see also Figures 4 and 5) contains rather less zirconium than the surrounding zircon particles, and yet its brightness indicates it is denser than most of them. X-ray analysis reveals the presence of rare-earth elements (REEs), specifically cerium and lanthanum (see Figure 10). It was not possible to collect Raman spectra using 514 nm excitation due to a strong fluorescence emission, but 785 nm excitation gave the spectrum shown in Figure 11.



Figure 9
Particle containing REEs

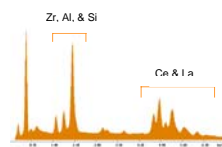


Figure 10
X-ray spectrum from particle indicated in Figure 9

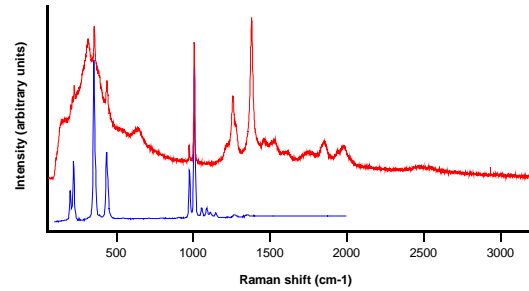


Figure 11
Raman spectrum (in red) collected from the particle shown in Figure 9, zircon reference spectrum in blue

The peaks from the zircon matrix (a zircon reference spectrum is shown in blue) are still apparent, but photoluminescence peaks from the REEs are superimposed over them.

Figure 12 shows another grain (coloured red), which from EDS analysis contains neither titanium nor zirconium, but calcium, magnesium, silicon and oxygen.

Raman analysis of this particle (Figure 13) gave a good match for **diopside** ($\text{Ca,MgSi}_2\text{O}_6$), one of the **pyroxene** group of minerals – this is consistent with the x-ray data.

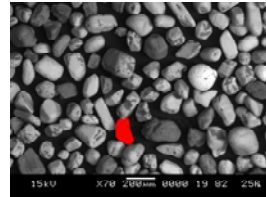


Figure 12
Particle containing Ca, Mg, Si, and O (no Ti or Zr)

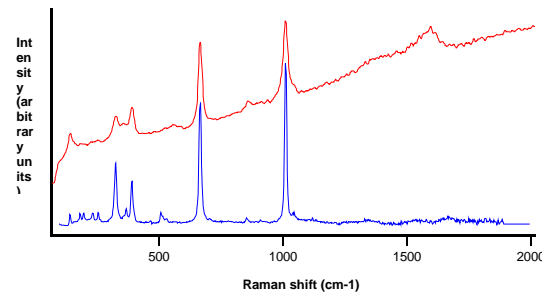


Figure 13
Raman analysis (in red) of particle shown in Figure 12, diopside reference in blue

In this study, combining SEM and EDS with Raman spectroscopy has enabled characterisation of the sand to be carried out more efficiently than by using the techniques in isolation. X-ray mapping can identify the elemental composition of dozens of grains simultaneously and quickly (a few minutes), key elements can then be used to classify the grains (see Figures 5 and 6 for example). Typical grains can then be analysed using Raman spectroscopy to determine their chemical and structural composition.

Image analysis of the x-ray maps is a trivial matter, and so it is possible to calculate a ratio for the number or volume of titanium containing grains in the zirconium stream, this can be used as a measure of the efficiency of the separation process.

The SEM/EDS technique is sensitive enough to detect grains that differ from the modal types, and these can be analysed individually using Raman spectroscopy to determine their chemical structure. Some of the grains may be commercially important (those containing the rare earth elements for example) so it is important they are not overlooked. The elemental composition provided by EDS can help to explain otherwise confusing spectral bands in the Raman spectrum.

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, cristobalite)
- 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
- Samples can be viewed with minimal preparation enabling them to be analysed by other methods
- Full characterisation of mineral mixtures 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.

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